Eastern Economy Edition

Thermodynamics

A Core Course

Third Edition

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THERMODYNAMICS: A Core Course, 3rd ed.
R.C. Srivastava, Subit K. Saha and Abhay K. Jain

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Preface

In the **third edition** of the book, a new chapter on "Causality Principle in Non-equilibrium Thermodynamics" has been added. Since the causality principle is at the core of philosophy of science and scientific method and temper, it is hoped that the readers will find this chapter intellectually stimulating.

Earlier in the **second edition,** two new chapters were added—Chapter 6 (The Question of Ideality) and Chapter 9 (The Non-linear Region)—to provide a more sense of completeness to the book. With the addition of Chapter 6, the portion of the book (Chapters 1–5 and 7) dealing with equilibrium thermodynamics became more useful to the students preparing for undergraduate/honours course in the subject.

Since many universities, at the postgraduate level, have introduced a course on non-equilibrium thermodynamics, the portion of the book (Chapters 7–10) with the addition of Chapter 9, dealing with non-equilibrium thermodynamics, is better equipped to cater to the needs of such a course.

The first author had joined the UGC Emeritus Fellowship during the period the second edition of the book was under preparation. He gratefully acknowledges the support from UGC.

Readers, particularly students, are encouraged to send their suggestions to us with regard to improvements in the contents and presentation of the book.

Authors

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Preface to the First Edition

There's no dearth of textbooks on thermodynamics. Hence, it is logical for any one to ask "why one more—what is the need?" We respect this question and offer our explanation as under:

Thermodynamics is neither engineering, nor physics nor chemistry nor biology. It is a tool used by all disciplines. Hence it is only proper that at least one course on thermodynamics is included in the programmes of study of all sciences and technologies. Now the major question that arises is that if in any programme of study only one course on thermodynamics is to be given, what should be the complexion of this course. Such a course in our opinion should aim at acquainting the student with the whole breadth of thermodynamics, i.e. thermodynamics in both equilibrium and non-equilibrium regions.

The present text, therefore, attempts to quickly acquaint the students with the complete complexion of thermodynamics. Thermodynamics in equilibrium and non-equilibrium regions along with the relatively more recent development of network thermodynamics are therefore included herein.

The book is organized into eight chapters. Chapters 1–6 deal with equilibrium thermodynamics while Chapters 7 and 8 discuss non-equilibrium thermodynamics.

In the present text, care has also been taken to accommodate the needs of existing syllabi. For example, Chapters 1–6 can cater to the needs of courses in thermodynamics prescribed for the undergraduate/honours courses. In most of the universities, non-equilibrium thermodynamics has been introduced at the postgraduate level for which no suitable text is available; some of the books available are of very advanced level. Chapters 7 and 8 are expected to serve the needs of courses on non-equilibrium thermodynamics at the postgraduate level. Chapter 8 on network thermodynamics is the most recent development in non-equilibrium thermodynamics for which no textbook is available; all the material presently available is in the form reviews and lecture note series. Since equilibrium thermodynamics is a prerequisite to gaining a good understanding of non-equilibrium thermodynamics, the entire material presented in the book has a sense of completeness and is expected to be useful to both teachers and students who want to teach and learn thermodynamics as a core course.

Absolutely no claim is made that the text is free from errors. In fact, there may be many, each one of which we would like to own and improve upon. For this we depend upon the readers, particularly students, whom we thank in advance.

Thanks are due to Prof. S. Venkateswaran, Director, Birla Institute of Technology & Science, Pilani and to Prof. G.P. Srivastava, Dean, Educational Development Division of the institute for their keen interest in this work. The present text was written during the period when the first author was working as an Emeritus Fellow under the AICTE scheme. He gratefully acknowledges this support. The authors thank Mr. Narendra Saini, Mr. Ashok Jitawat and Mr. Ajay Soni for word processing the manuscript and Mr. K.N. Sharma for the artwork.

Last but not the least, we thank the publisher, Prentice-Hall of India, especially its editorial and production teams, for careful processing of the manuscript at all the stages.

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Chapter 1

The Nature and Scope of Thermodynamics

Thermodynamics, as pointed out by Guggenheim in his celebrated book [1], is a misnomer. As the name indicates, time should also enter as a parameter in the structure of thermodynamics, which it does not particularly in the classical thermodynamics of closed systems based on the concept of equilibrium. Guggenheim, therefore, has also suggested, 'thermostatics' or 'thermophysics' as more appropriate names. A change of name, however, will serve no useful purpose because all these years whenever we said 'thermodynamics' we understood 'thermostatics'. As is well known, in dealing with open systems, which utilizes the concept of 'steady state' instead of 'equilibrium' time does enter as a parameter and 'thermodynamics' would be the appropriate name in such situations. In the present course it is intended to acquaint the students with both 'thermostatics' and 'thermodynamics'. We are sorry, we have used the technical terms like equilibrium, steady state etc. without introducing them. It will be done in a short while from now.

1.1 THE NATURE OF THERMODYNAMICS

Thermodynamics is neither engineering, nor physics, nor chemistry, nor biology. It is a tool used by all. This is why at least one common course on thermodynamics should be taken by all science and engineering students. As Professor Katchalsky[1] puts it, thermodynamics occupies the same place in sciences as logic in humanities. It is based on a limited number of axioms and the rest of it is just deductions from these axioms. These axioms are derived from everyday experience. For example, the first law of thermodynamics is just another statement of the principle of conservation of energy; energy cannot be created out of nothing, it can only be transformed. Similarly the second law: one hundred per cent conversion of heat into work is not possible. In fact, historically, these axioms are negative statements expressing failure of human efforts. Man tried to create energy out of nothing and failed and stated his experience in the form of the first law. He then tried to achieve the next best, i.e. no wastage in the conversion of heat to work. Failure in this endeavour led to the statement of the second law.

1. Please see the selected bibliography at the end of the book.

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Thus, the laws of thermodynamics are primarily empirical in nature, which in turn make thermodynamics an empirical science. This, however, calls for some comments. The theoretical rationale for these axioms derived from experience, would certainly lie in the happenings at the microscopic level (kinetic theory). One approach, therefore, could be to start with mechanics and then deduce the axioms of thermodynamics. Such an approach would not only remove the stigma of 'empirical science' from thermodynamics but would logically link kinetics, thermodynamics and statistical thermodynamics. Discussion on the basis of this approach is beyond the scope of this course. Nonetheless, the inquisitive student may refer to the book of Waldram, for such a discussion.

Thermodynamics is concerned with energy and energy changes. No wonder the principle of conservation of energy is its first axiom. What is the more important is the fact that it is unconcerned with the happenings at the microscopic level. It is, therefore, often boasted that results of thermodynamics are quite general and independent of any molecular model. True, this is an advantage but this is a disadvantage, too. That means thermodynamics alone cannot give the complete information. For complete information, therefore, one has to couple kinetic theory with thermodynamics. This is how and why statistical thermodynamics makes appearance. Thermodynamics can give information about the system when it is in a state of equilibrium; a time-invariant situation. Information about the approach to equilibrium is not within its purview; this is kinetics. The values of the properties of a system at equilibrium that one gets from thermodynamic considerations are always average values. This is natural because thermodynamics does not concern itself with the happenings at the molecular level; it does not concern itself with individual atoms and molecules of which the system is composed. Thermodynamics concerns itself with the system as a whole. Thus thermodynamic approach, in a way, is systems approach.

In the structure of thermodynamics the number of experimentally measurable quantities are a few whereas the number of correlations among the properties of the system are many. Thus by performing only a few experiments one can gain knowledge about several properties because of existing correlations. Temperature, for example, is one major experimentally measurable quantity. If we look closely, temperature also is not a directly measurable quantity. What one actually measures is either the length of the mercury column (if he is using a mercury thermometer) or electrical potential difference (if he is using a thermocouple or electrical resistance), if he is using a thermister. Temperature is only correlated with these properties.

1.2 LIMITATIONS AND SCOPE

One major limitation of thermodynamics is the concept of equilibrium itself. All thermodynamic correlations, results and quantities relate to the situation when the system has attained equilibrium while true equilibrium is never realised in practice. Or if we want to make a safe statement, we would say that a true equilibrium is attained only in infinite time. If we want a system to attain

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equilibrium all that we have to do is to allow the system to age. In fact equilibrium, like perfect gas, is just an idealized concept and exists only in our imagination.

The thermodynamics which bases itself on the concept of equilibrium may be called 'equilibrium thermodynamics'. The *equilibrium thermodynamics* can deal only with closed systems and isolated systems. The thermodynamics of non-equilibrium systems, on the other hand, bases itself on another time-invariant situation called 'steady state'. This thermodynamics is also called *thermodynamics of steady state* or *non-equilibrium thermodynamics*. In this book our intention is to acquaint the students with both equilibrium and non-equilibrium thermodynamics. The equilibrium thermodynamics will be dealt with first because its understanding is a prerequisite to the understanding of non-equilibrium thermodynamics.

We have so far been guilty of using technical terms without introducing them to the readers. In the next chapter, the technical terms used in the formalism of thermodynamics will be introduced and discussed.

QUESTIONS

1. Is thermodynamics is the right name; if not why? Please suggest a right name.
2. Should thermodynamics be classified as an empirical science. If yes, why?
3. The number of directly measurable quantities in thermodynamics are (i) one (ii) two (iii) three or (iv) zero, i.e. none. Choose the right answer.
4. True thermodynamic equilibrium is attained in (i) finite time (ii) infinite time. Choose the right answer.
5. Thermodynamics concerns with (i) happenings at the molecular level, (ii) the system as a whole. Choose the right answer.

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Chapter 2

Important Terminologies in Thermodynamics

Every discipline in the process of its development generates its own jargon. Thermodynamics is no exception. We will introduce and discuss here some of the technical terms (not all), necessary for going ahead with the subject.

2.1 THE SYSTEM

The primary objective of science is to understand the world around us with a view to using it to our advantage. Since it is just not possible to make observations on the whole world at a time, it has been customary in science to extract relevant portions of the world and put them under observations. These relevant extracts of the physical world separated from the rest of the world by means of well-defined boundaries are called *systems*. Whatever is left out is called *environment* or *surroundings*. Thus, the whole world may be divided into two parts, 'system' and its 'environment'. Thus, a system is based on our choice. One is at a perfect liberty in the choice of a system depending upon what analysis he intends to perform on it. For example, when 'motion' is involved, a frame of reference, in which to measure the movement, may be a part of the system.

If 'mass' is held constant the system is called a *closed system*. In engineering textbooks it is mentioned as *control mass system*. In fact the 'closed' and the 'control mass system' are the same things. In this book we will use the term 'closed system'. The surrounding walls of a closed system must not permit any material transport across them. Although mass of a closed system remains constant, but the energy may vary. This implies that surrounding walls though impermeable to matter, should be permeable to energy. This fact further implies that the walls would be made of good conductors; good conductors of heat, electricity, etc. As we will see later, the energy of a closed system can also be varied either by doing work on it or by extracting work from it, the walls of the closed system should also be elastic so that the system may expand or shrink depending upon the situation.

If the enclosing walls are impermeable to both matter and energy, the system is said to be an *isolated system*. It is easy to see that the enclosing walls of an isolated system should be impervious, rigid and made of non-conducting materials. Whatever may be the mechanism an isolated system is not supposed to

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interact with its environment in any way—neither in terms of transport of mass nor in terms of transport of energy. The concept of an isolated system is highly idealized and resides only in our imagination. One of the nearest approaches to an isolated system is a Dewar flask. We know that a hot drink does not remain hot indefinitely in a Dewar flask. The isolated system though highly idealized and practically unattainable is a useful concept in performing energy analysis because system plus environment can always be taken as an isolated system. The mass and energy of an isolated system remain constant because it does not interact with its environment in terms of both mass transfer and energy transfer.

If a system communicates with its environment in terms of both, mass transfer and energy transfer, it is called an *open system*. For example, human body is an open system. Open systems will be dealt with in detail in Chapters 8 and 10. (Please bear with us till then!)

There are several adjectives in addition to 'closed', 'open' and 'isolated' which are used to qualify systems further. These are, for example, *isothermal* meaning same temperature, *isobaric* meaning same pressure, *adiabatic* meaning no exchange of heat with the environment, *isochoric* meaning no change of volume, etc. Thus an isothermal system would mean a system at constant temperature and so on. These adjectives can also be used to qualify a process, e.g. an isothermal process. A healthy human body is an isothermal open system.

Without spending much time on this kind of grammar let us think over the question of defining a system. Suppose we have taken some fluid in a container and we want that someone at a far off place, who is not able to come and see the system himself should duplicate this system. We should write to him giving complete description of the system. The question is what shall we tell him so that he gets a complete description of the system in order to be able to duplicate it. In addition to what fluid we have taken, we should tell its mass, its density, what volume does it occupy and at what temperature and pressure, etc. It is easy to see that only a few of these variables are independent. For example, if the fluid behaves ideally, any two of the three variables, pressure, volume and temperature, are independent. The minimum number of independent variables necessary for complete description of the system are called *state variables*; the complete description is said to define the state of the system. The next question that crops up is that how does one arrive at this figure—the number of independent variables necessary to define the state of a system. Do we have to always follow the method of inspection, i.e. make a list of all possible variables and then shortlist the independent variables by inspection or there is some rule based on thermodynamic rationale to arrive at this minimum number of independent variables. There is a rule for determining the minimum number of independently variable thermodynamic properties for defining the state of a system. We will take it up after we have introduced the first law of thermodynamics. (Bear with us till then!)

State variables in fact are mostly the experimentally determinable properties of a system. Property is an attribute which belongs to a system and which can in principle be quantitatively evaluated. One should always keep in mind that context is very important when he talks of properties. Property should be relevant to the context. For example, how beautiful is a girl, is not a relevant property in

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the context of her winning a judo match; in the context of a judo match the relevant property is her agility. Similarly, when we are talking thermodynamics the relevant properties are energy, volume, temperature, pressure, etc. Remember, heat and work are not properties; they do not belong to the system. These are operations, which are performed on the system to alter its energy. In thermodynamics the central theme is energy and energy transfer. The relevant properties are, therefore, those that are involved with energy in some way.

2.2 EQUILIBRIUM AND STEADY STATE

Let us take some water in a beaker at, say 80°C while the room temperature is, say 30°C. If we monitor the temperature of the water in the beaker with time, the temperature of the water will fall with time till it becomes equal to the room temperature. From this time onwards the temperature of the water in the beaker would remain constant provided the temperature of the ambient does not change. This is a time-invariant situation. Now let us take up the famous Searl's experiment of thermal conductivity which you must have read in your school physics. Let us think of a metallic rod which is being heated at one end and in which several thermometers are inserted along its length (Figure 2.1). If we monitor the temperatures in the various thermometers (T_1, T_2, T_3, T_4 and T_5) with time we will notice that temperature in each of the five thermometers will increase with time. A state will be reached when temperatures as recorded in the thermometers will become invariant with time though the temperature in each thermometer will be different and will be higher than the temperature of the ambient. This is another time-invariant situation.

A closer scrutiny will reveal that the two time-invariant situations are entirely different from each other. In the first time-invariant situation one has to do nothing;

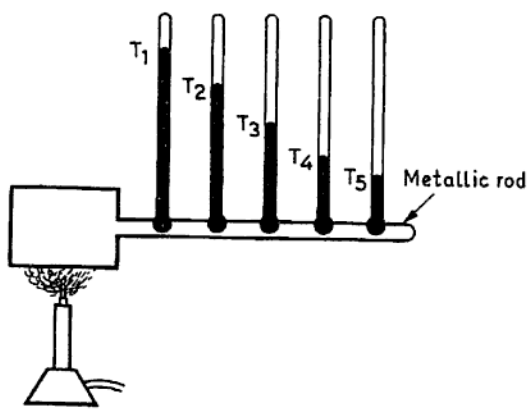

Figure 2.1 Steady state.

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he has to leave the system to itself and wait, whereas in the second time-invariant situation (the Searl's experiment, Figure 2.1) a continuous supply of heat is required. The major point of difference is that the first time-invariant situation is the natural tendency of the system; it is a natural situation. The second time-invariant situation, however, is an artificial situation or a forced situation, where a continuous supply of energy is required. The former time-invariant situation is called *equilibrium* while the latter is called a *steady state*. The prime difference between an equilibrium state and a steady state is that the former is a natural situation and one does not have to spend any energy to attain it while the latter is an artificially forced situation and to attain it a continuous supply of energy is required. It is also easy to see that a steady state, though an artificial situation, is more comprehensive than equilibrium; equilibrium state is only a subset of steady state. Consider once again the Searl's experiment (Figure 2.1). What will happen if we put off the burner? All the five thermometers will ultimately record the same temperature which will be equal to the temperature of the ambient, i.e. the system will attain equilibrium. This example brings home the point that equilibrium state is a particular case of steady state. Let us take a very common example to illustrate this point. A healthy human body maintains a constant temperature of around 37°C, which does not depend on the temperature of the ambient. This indeed is a time-invariant situation which is an artificial situation or a forced situation. It is a steady state. One has to spend a lot of money for the continuous supply of energy in the form of food to maintain this time-invariant situation (try to remember your mess bill). What will happen if one cuts off the supply of this energy, i.e. stops taking food? This situation is similar to the situation when the burner was put off in the Searl's experiment (Figure 2.1). The answer is simple. Death will occur and the temperature of the dead body will not be 37°C and independent of the temperature of the ambient. It will, however, remain constant provided the temperature of the ambient remains constant. This time-invariant situation is equilibrium. Thus life is steady state and death is equilibrium. Life is an artificial situation and has to be forced whereas death is natural. Steady state will be utilized in the discussion of thermodynamics of open systems, whereas equilibrium states will form the basis of thermodynamic discussion of isolated systems and also of closed systems. In spite of the sharp difference between equilibrium state and the steady state, the attribute common to both of them is that the system shows no further tendency to change its properties with time.

To illustrate the concept of equilibrium further let us take a simple mechanical example. Let us look at Figure 2.2, where a solid block is shown resting on a table. Of the three positions the solid block is said to be in equilibrium in positions *A* and *C*; the equilibrium at *C* being the stablest. The position *C* is the stablest equilibrium because the centre of gravity of the block is at the lowest in this position, i.e. the potential energy is minimum. For a more quantitative idea, let us plot potential energy of the system as a function of the position of the centre of gravity. The minima at *A* and *C* in the curve, Figure 2.2 (b), represent the positions of equilibrium—lower the value of potential energy stabler the equilibrium. The maximum at *B* in the curve represents an unstable situation; in fact it is called *unstable equilibrium.*

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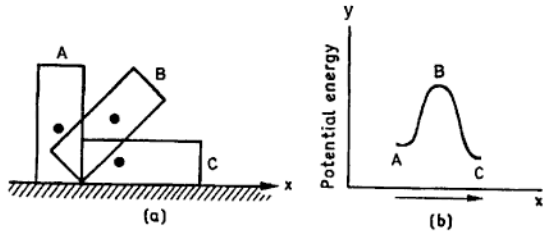

Figure 2.2 State of equilibrium. Centre of gravity is lowest in position *C*.

The criterion that for mechanical systems in equilibrium the potential energy should be minimum is not totally irrelevant for physico-chemical systems. Similar principles will be found to apply in more complex physico-chemical systems. In addition to purely mechanical changes, such systems may undergo temperature changes, changes of state of aggregation and chemical reactions. The problem of thermodynamics is to discover or invent new functions that will play a role in more general systems that a potential energy plays in mechanics.

2.3 ENERGY

Energy is a property of the system. It is an attribute which belongs to the system. The total energy of a system can be divided into two components. First, (i) the energy inherent in the system. This energy is on account of the atoms and molecules and the fashion in which these atoms and molecules are correlated with each other in the matter comprising the system. Since atoms and molecules are in a constant state of random motion, this energy ultimately comes from the mechanical energy of atoms, molecules and the constituent fundamental particles, and hence can be said to be the energy corresponding to hidden microscopic modes. This is called *internal energy* of the system. The other component is (ii) the macroscopic energy imparted to the system. This is the bulk or the macroscopic energy (kinetic, potential, etc.). For example, one can take a chunk of coal and throw it with a velocity v or lift it to a height h from the ground and thus impart the bulk kinetic energy or bulk potential energy to the chunk of coal.

The internal energy U is random in nature and by itself cannot be put to useful work. For example, if we take water in a beaker and keep it in contact with coal, the water does not get heated up inspite of the fact that coal has internal energy. The reason is simple; the internal energy of the coal is random or disorganized or disordered energy. In fact, the major task of all technologists is to convert this kind of random energy into ordered energy.

Thus the total energy (E) of a system can be written as:

$$E = \underset{\substack{\text{(Bulk kinetic}\\ \text{energy)}}}{\text{KE}} + \underset{\substack{\text{(Bulk potential}\\ \text{energy)}}}{\text{PE}} + U + \text{Any other form of bulk energy}$$

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2.4 EXTENSIVE AND INTENSIVE PROPERTIES

Extensive properties as the name indicates are those which depend on the extent of a system. These properties are additive and are also called *capacity factors*. The common example is 'mass'. *Intensive properties* as the name indicates are related to the intensity and are not additive. The common example is 'temperature'. If we mix 1 kg of water at 100°C with 1 kg of water at 40°C, the temperature of the mixture will not be 140°C. Such properties are also called *intensity factors*.

2.5 STATE FUNCTIONS

As mentioned earlier the thermodynamic properties (e.g. pressure, temperature, volume, internal energy, etc.) are utilized to fix the thermodynamic state of a system and hence are also called *state functions*. Once we call them state functions the obvious implication is that these properties are determined by the thermodynamic state of the system and not on how this state is reached. Let us take a simple example. Suppose we want to travel from point A to point B on the x-y plane (Figure 2.3).

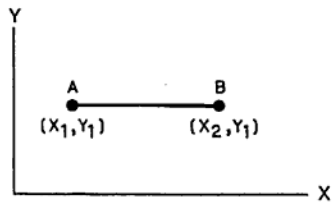

Figure 2.3 State functions.

The points A and B are analogous of the two states and the position coordinates (x_1, y_1) and (x_2, y_1) are the analogue of the pair of state functions defining the two states. One may follow innumerable paths to reach B from A, but the position coordinates of B would always remain the same irrespective of what path one follows. However, the fatigue one feels in going from A to B will depend upon the path, i.e. the work done will be determined by the path. The value of the difference between the position coordinates x and y corresponding to the states A and B will also remain the same whatever may be the path between A and B. The message that is driven home is that state variables depend only on the state of the system and not on the way they are arrived at.

In the language of calculus, state functions give exact differentials which can be integrated within limits without regard for the actual change that occurs as the system moves from one limiting condition to another. To clarify matters, let us write

$$Z = Z(x, y) \tag{2.1}$$

or

$$dZ = M(x, y)\, dx + N(x, y)\, dy \tag{2.2}$$

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where

$$M(x, y) = \left(\frac{\partial Z}{\partial x}\right)_y \quad \text{and} \quad N(x, y) = \left(\frac{\partial Z}{\partial y}\right)_x \tag{2.3}$$

If dZ is an exact differential, it simply means that Z is a continuous function of the two independent variables x and y. Therefore

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{2.4}$$

The order in which the second partial derivative is taken is unimportant. Equation (2.4) is the Euler's reciprocity relation and is quite useful. The relationship

$$\frac{\partial^2 Z}{\partial y \partial x} = \frac{\partial^2 Z}{\partial x \partial y} \tag{2.5}$$

automatically follows from Equation (2.4). As we will see later, applying the concept of exact differentials to the state variables like internal energy, enthalpy, Gibbs' free energy function and the Helmholtz function and using Euler's reciprocity relations, one gets the four useful Maxwell's relations. These will be dealt with in Chapter 5.

2.6 WORK

The concept of *work* comes from mechanics. The basic definition of work (W) is that

$$W = \int_1^2 F\,dx \quad \text{or} \quad dW = F\,dx \tag{2.6}$$

where F is the force acting in the direction of the displacement dx of the particle. To clarify the definition, let us consider the example of a gas enclosed in a cylinder fitted with a movable piston, as in Figures 2.4(a) and (b).

Let us first consider the expansion process and fix up the origin of coordinate axes at O, the initial position of the piston. As a result of the force exerted by the

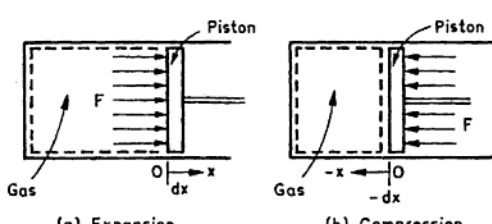

Figure 2.4 Work of expansion and compression.

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gas, the piston moves forward by a distance dx. The work done dW in the situation is equal to $F\,dx$. The questions that should be asked at this stage are: (i) who does this work and (ii) on whom this is being done. The answers are simple. The work is done by the gas on the piston. If the gas is taken to be the closed system and piston a part of the environment, the above answers should be reworded as: the work is done by the system on the environment. Now let us consider the case of compression and fix up the origin of coordinate axes at O, the initial position of the piston. As a result of the force F exerted by the piston, which is a part of the environment, on the gas, which is our system. The boundary of the system is pushed in by a distance, $-dx$. The movement of boundary in the case of compression is opposite to that in the case of expansion. Thus the work done by the environment on the system is $-F\,dx$. Thus recalling that pressure P is the force F per unit area A of the cross-section on which the force acts, we can write that in the expansion process, work is done by the system and is given by

$$dW = F\,dx = \frac{F}{A}A\,dx = P\,dV \tag{2.7}$$

and in the compression process, work is done on the system and is given by

$$dW = -F\,dx = -\frac{F}{A}A\,dx = -P\,dV \tag{2.8}$$

where dV is the change in volume.

Now, let us remember an everyday experience. When we inflate our bicycle tyres, the bicycle pump gets heated up; in fact it is the air in the pump that gets heated up. It is not difficult to see that when we pump in the air the work is being done on the gas. Similarly, when a gas is expanded it gets cooled down. In fact, adiabatic expansion is one of the common methods of producing low temperatures. These observations in thermodynamic terminology lead us to the following statements: When work is done on the system, system gains energy and when work is done by the system the system loses energy. In fact, these statements are generally valid where work of any kind, mechanical, electrical, etc, is done on the system or by the system. That is, whenever work is done on the system the system gains energy and whenever work is done by the system, the system loses energy. There is another important message contained in these statements: Work is a mode of energy transfer, i.e. by doing work on the system or taking work from the system we can alter the energy of a closed system. Thus work is an *operation*, which is performed on the system and not a *property* of the system. This also implies that work (dW) is not a perfect differential (its value depends on the path), i.e. how the work is performed. The following simple example will illustrate the point. Suppose for a system consisting of a gas contained in a piston–cylinder arrangement, on a P-V plane we want to go to the final state 2 from the initial state 1, as in Figures 2.5(a) and (b).

One can reach the final state 2 from the initial state 1 by following several paths, two of which are shown in Figures 2.5(a) and (b). It is easy to see that the work done is different in the two cases (shaded area in Figure 2.5 is the magnitude of the work done).

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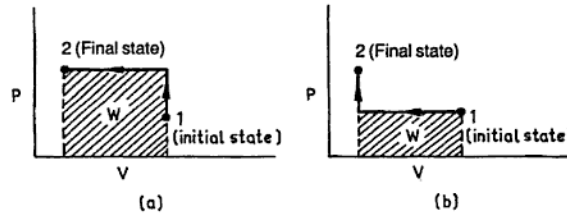

Figure 2.5 Path-dependence of work.

There is another way of looking at this issue. The integral

$$W = \int_1^2 F\,dx \tag{2.9}$$

cannot be worked out unless some restrictive condition, e.g. F = constant is imposed on the system or a functional relationship between F and x is discovered. This means that dW in general is not integrable. This is consistent with the statement that dW is not an exact differential.

2.7 HEAT AND TEMPERATURE

Heating-like work is also an operation, which is performed on a system to alter its energy. Let us visualize what happens when we heat a system. The constituents atoms and molecules as a result of the supply of heat would start moving at random with higher speed and would collide with each other and thus increase the energy of the system. Thus heat can be identified with mechanical motion of atoms and molecules at a microscopic level. We can also visualize heat as energy transfer as work on the microscopic scale which fails to be accounted for by macroscopic evaluation of the work.

As a corollary to this, according to kinetic theory, temperature is a measure of the average translational kinetic energy E_K of the molecules, i.e.

$$T = T(E_K) \tag{2.10}$$

Therefore, the lowest conceivable temperature would be the one at which all molecular motions cease. Such a temperature is called *absolute zero* of temperature. However, this is a different question whether absolute zero of temperature is experimentally attainable. It is not experimentally attainable. The absolute zero of temperature though resides only in our imagination is quite an important concept. Among other things, it gives us a basis of measuring temperature and drawing up a scale for temperature measurement. This is how temperature is viewed in the kinetic theory. Its thermodynamic interpretation will be taken up a little later.

Let us once again emphasize that heat and work are nowhere stored in the system; they do not belong to the system and hence are not properties of the system. These are operations which are performed on the system. Temperature on the contrary belongs to the system and hence is a property of the system.

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2.8 HEAT CAPACITY

Heat capacity of a substance is the ratio of heat supplied to it to the rise in its temperature. A little consideration would show that this definition can mislead us. Consider a definite amount of gas, at room temperature, contained in a cylinder fitted with a movable piston. If the piston is pushed in suddenly the temperature of the gas would rise. The ratio of heat supplied to the rise in temperature (heat capacity) in this situation is zero.

Let us now perform another experiment. Now, suddenly pull the piston out. As a result, temperature of the gas will fall. After the temperature has fallen below the room temperature let us start heating the gas till it comes back to its original temperature. In this experiment, the heat supplied to the system is finite though the rise in temperature is zero. In this situation therefore the ratio of heat supplied to the rise in temperature would be infinite. Thus the heat capacity of the gas can have any value between zero and infinity depending upon how the experiment for its evaluation has been performed. Such a situation cannot be tolerated. Hence it has become customary to talk of heat capacity under restrictive conditions. The restrictive conditions are constant pressure and constant volume. The heat capacity at constant pressure and the heat capacity at constant volume are represented as C_P and C_V respectively. It is well known that C_P is generally greater than C_V. The more rigorous thermodynamic approach to C_P and C_V will be presented in the next chapter. It will be seen that in the case of incompressible substances, C_P and C_V are more or less equal. In the differential form, we can express

$$C_P = \frac{(dQ)_P}{dT} \tag{2.11}$$

and

$$C_V = \frac{(dQ)_V}{dT} \tag{2.12}$$

$(dQ)_P$ and $(dQ)_V$ are heat supplied at constant pressure and constant volume respectively.

EXAMPLE 2.1 The temperature of 25 g of water vapour increases by 9.69 K when 0.45 kJ of heat is supplied at constant pressure. What is its molar constant pressure heat capacity, if it behaves as a perfect gas,

Solution We know

$$dQ_P = nC_P\, dT$$

$$0.45 \times 10^3\ \text{J} = \frac{25\ \text{g}}{18\ \text{g/mol}} \times C_P \times 9.69\ \text{K}$$

Therefore,

$$C_P = \frac{0.45 \times 10^3\ \text{J} \times 18\ \text{mol}^{-1}}{25 \times 9.69\ \text{K}} = 33.44\ \text{JK}^{-1}\text{mol}^{-1} \quad \blacksquare$$

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2.9 REVERSIBLE PROCESSES

Reversible process as the name indicates is the one that can be reversed. This simplistic definition has quantitative elements in it and has important implications. One should be able to reverse the process along the same path. Also, all the effects which are observed in the direct process should be quantitatively reversed in the reverse process. For example, if in going from state 1 to state 2, Q units of heat is evolved then in going from state 2 to state 1 along the same path Q units of heat should be absorbed. There are several attributes which follow as a consequence of reversibility. A reversible process is the most efficient process. Work obtained from a system in going from state 1 to state 2 via a reversible path is the maximum possible work obtainable from the system. All the intermediate points between the states 1 and 2 (which are already equilibrium states) along a reversible path are also equilibrium states. In other words, a reversible path is the one connecting intermediate states, all of which are equilibrium states. Since an equilibrium state is (ideally) reached in infinite time a reversible process must in limit be performed (infinitely) slowly. The change should be gradual so that every state is only infinitesimally different from its neighbouring state. Thus reversible process is another idealized concept which resides only in our imagination. Nevertheless, it is an extremely important concept in thermodynamics as we will see later.

EXAMPLE 2.2 Calculate the minimum work which must be done to compress 16 g of oxygen at 300 K from a pressure of 1 atm to a pressure of 100 atm. Assume the ideal gas behaviour for oxygen ($PV = nRT$).

Solution Since it is required to calculate the minimum work of compression, the change should be reversible, i.e. the gas should be compressed very slowly by gradual increase of pressure so that equilibrium prevails at every part in the path of the process and every state is only infinitesimally different from its neighbouring state. Then

$$W = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = -2.303nRT \log \frac{V_2}{V_1}$$

where

$$n = \frac{16}{32} = 0.5, \qquad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}, \qquad T = 300 \text{ K}$$

Hence,

$$\begin{aligned} W &= -2.303 \times \frac{1}{2} \times 8.314 \times 300 \log \frac{V_2}{V_1} \\ &= 2.303 \times \frac{1}{2} \times 8.314 \times 300 \log \frac{P_2}{P_1} \\ &= 2.303 \times 8.314 \times 300 \times 2 \times \frac{1}{2} \\ &= 5744 \text{ Joules} \quad \blacksquare \end{aligned}$$

Reversible work done on the gas = 5744 Joules.

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2.10 SIGN CONVENTION

The sign convention in thermodynamics is the same as in everyday life in the context of gain and loss. The plus sign indicates gain and the minus sign indicates loss. The gain of heat by the system is written as positive and the loss as negative. Let us take an example. When we hold by hand a beaker containing some water and then add some sulphuric acid to it, our palm gets warmed up. In this case, heat comes to the palm, which is part of the environment, form the water and sulphuric acid in the beaker, which is our system. Thus the system loses energy and the environment gains. This is why the heat of all exothermic processes is written as negative. By a similar argument, heats of endothermic process are written as positive. We have already stated (refer to the section dealing with work) that whenever work is done on the system, the system gains energy and whenever work is done by the system, the system loses energy. Therefore, the work done on the system should have a positive sign and the work done by the system should be given a negative sign.

Familiarity with the above terminology makes it convenient for us to discuss the first law of thermodynamics and its applications. This would form the subject matter of the next chapter.

QUESTIONS

1. Give one example each of (a) a closed system (b) an open system and (c) an isolated system.
2. Energy of an isolated system can be altered (i) by doing work on the system (ii) by extracting work from the system (iii) by heating or cooling the system (iv) cannot be changed at all. Choose the right answer.
3. Internal energy is (i) disorganized energy (ii) organized energy (iii) none of these. Choose the right answer.
4. A naughty boy hit a bird with a stone and the bird was injured. The injury was caused by the transfer of internal energy of the stone to the bird. What is wrong with the statement.
5. In the case of an exothermic process the heat of the process is written as negative even though a positive heat is evolved from the system. Why?
6. What is wrong with the following statements: (i) The energy of the system was lost (ii) The energy was dissipated into heat (iii) Work of the system is so much (iv) Heat of the system is so much.
7. Internal energy of 5 g of water is (i) greater than 5 g of ice (ii) equal to 5 g of ice (iii) less than 5 g of ice. Which one of these is the right answer and why?
8. When a man moves on the road some work is being done. Who does this work and on whom the work is being done.

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9. Mr. Asis Das walked, with his baggage weighing 10 kg, through the shortest distance of 10 km from his residence to Howrah railway station to catch a train. On reaching the railway station he found that the train had left and therefore returned through the same route on foot with his baggage. If the bodyweight of Mr. Das is 100 kg, estimate the total amount of work done in the process of to and fro movement. This work was done by whom and on whom?
10. (a) How much time does it take to perform a process reversibly: (i) finite (ii) infinite? (b) How much time is required for a system to attain true equilibrium: (i) finite (ii) infinite? Choose the right answers.

EXERCISES

2.1 For 1 mol of an ideal gas, calculate the work done by the gas on the surroundings if it undergoes a reversible isothermal expansion at $T = 400$ K whereby the pressure changes from 1.0 bar to 0.5 bar. Repeat the calculation if the gas then goes from 0.5 bar to 0.25 bar and then again if it goes from 0.25 bar to 0.125 bar.

2.2 The temperature of 2 mol of argon gas increase by 5.85 K when 350 J of energy is supplied as heat. Calculate the molar heat capacity at constant volume and constant pressure of the gas.

2.3 Thirty gram of ethane occupies 25 L at 300 K. What would be the work done if the gas expands isothermally and reversibly when the volume of the gas increases by 5 L?

2.4 A gas is confined in a container of volume 15 L at 300 K. What is the work done when the gas expands isothermally and irreversibly against a constant external pressure of 3×10^4 Pa until its volume has become 18 L?

2.5 Prove that in case of one mole of a van der Waals' gas the work done in isothermal reversible process is

$$W = RT \ln \frac{V_2 - b}{V_1 - b} + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

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Chapter 3

The First Law of Thermodynamics

3.1 BALANCE SHEET OF ENERGY TRANSACTIONS

The first law of thermodynamics is in fact a balance sheet of energy transactions. It is an extension of the principle of conservation of energy. To illustrate this point, let us consider a closed system whose energy we want to alter. This can be achieved through heat operation or work operation or both. If heat (Q) is supplied to the system and a work (W) is done on the system the consequence will be that energy (E) of the system will increase. The situation is pictorially depicted in Figure 3.1.

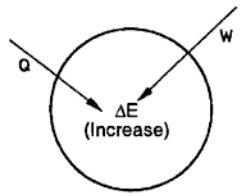

Figure 3.1 Operations being done on a closed system for altering its energy.

The balance sheet can now be written as

$$Q + W = \Delta E \text{ (increase in energy)} = E_{\text{final}} - E_{\text{initial}} \tag{3.1}$$

The positive signs with Q, W and E indicate a gain by the system. If heat is supplied to the system and a work is done by the system, as a consequence, energy of the system increases, Q and ΔE in Equation (3.1) will be positive and W will be negative, i.e.

$$Q - W = \Delta E \tag{3.2}$$

In the differential form, Equation (3.1) can be written as

$$dQ + dW = dE \tag{3.3}$$

If internal energy (U) is the only energy the system has, Equation (3.3) gives

$$dQ + dW = dU \tag{3.4}$$

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Equations (3.1)–(3.4) are quantitative statements of the first law of thermodynamics. The two examples given below would illustrate the first law analysis.

EXAMPLE 3.1 Two kilogram of a gas is squeezed in a piston–cylinder arrangement from 14 m^3 to 9 m^3. During this operation the pressure is kept constant as 2000 Nm^{-2}. If the internal energy of the system decreased by 6000 J, calculate how much energy was transferred as heat to or from the gas in this process.

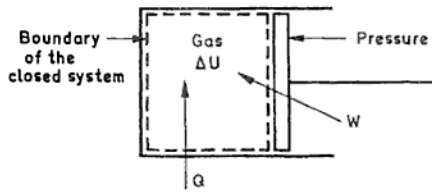

Figure 3.2 A closed system showing inputs Q and W.

Solution The process can be represented as shown in Figure 3.2. From the first law, we can write

$$W + Q = \Delta U \quad \text{(increase)}$$

where

$$W = \int_1^2 -P\,dV = P(V_1 - V_2) = (2{,}000\ \text{Nm}^{-2})(14 - 9)\ \text{m}^3$$

$$= 10{,}000\ \text{Nm}$$

$$= 10{,}000\ \text{J}$$

and

$$\Delta U = -6{,}000\ \text{J}$$

Therefore,

$$10{,}000\ \text{J} + Q = -6{,}000\ \text{J} \quad \text{or} \quad Q = -16{,}000\ \text{J}$$

The negative sign indicates that the system loses heat. Hence the direction of Q should be opposite to what has been shown in Figure 3.2. ■

EXAMPLE 3.2 One mole of an ideal gas (obeying $PV = nRT$) is expanded isothermally at 27°C and reversibly—the initial and final volumes being 2.28 m^3 and 4.56 m^3. If the internal energy of the ideal gas is a function of temperature only, calculate the heat lost or gained by the system. Given the gas constant $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$.

Solution From the first law, we can write

$$Q + W = \Delta U$$

Since this is the case of expansion, W will be negative. Further since $U = U(T)$ for ideal gases $\Delta U = 0$ for the process. In view of these considerations

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$$Q - W = 0 \quad \text{or} \quad Q = W$$

$$Q = W = \int_1^2 P\,dV = \int_1^2 \frac{RT}{V}\,dV = RT \ln \frac{V_2}{V_1}$$

$$= 2.303\,RT \log \frac{4.56}{2.28}$$

$$= 2.303 \left(8.314 \text{ JK}^{-1} \text{ mol}^{-1}\right)\left[(27+273) \text{ K}\right] \log 2$$

$$= 1729 \text{ J mol}^{-1}$$

The work done by the gas equals heat absorbed by the gas from its environment. ■

3.2 HEAT CHANGE AT CONSTANT PRESSURE—ENTHALPY

Writing first law for a closed system with inputs of heat and mechanical work under constant pressure and assuming that internal energy is the only energy the system has, we can write

$$Q + W = \Delta U = U_2 - U_1 \tag{3.5}$$

Since W is the mechanical work done on the system under constant pressure the first law can be rewritten as

$$Q_P + P(V_1 - V_2) = U_2 - U_1$$

or

$$Q_P = (U_2 + PV_2) - (U_1 + PV_1) \tag{3.6}$$

where U_1, V_1 and U_2, V_2 represent the internal energy and volumes at the initial state 1 and at the final state 2, respectively. Thus, it is clear from Equation (3.6) that the heat supplied to the system at constant pressure is equal to the difference between the functions $(U + PV)$ at the final and at the initial states. The function $(U + PV)$ is denoted by H and is called *enthalpy* or *heat content*. Thus

$$Q_P = H_2 - H_1 = \Delta H \tag{3.7}$$

EXAMPLE 3.3 The latent heat of vaporization of bromine is 29.2 kJ/mol at 59°C and 1 atm pressure. Find out Q, W and ΔU when 1 mole of bromine vaporizes.

Solution Latent heat of vaporization is

$$\Delta H = Q_P = 29.2 \text{ kJ mol}^{-1}$$

and

$$W = -P\Delta V$$

$$= -P\left(V_{\text{gas}} - V_{\text{liquid}}\right)$$

$$\approx -PV_{\text{gas}}$$

$$= -RT$$

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$$= -8.314 \times 10^{-3}\ \text{kJK}^{-1}\ \text{mol}^{-1} \times 332\ \text{K}$$

$$= -2.76\ \text{kJ}$$

Then

$$\Delta U \mp Q + W = Q_P + W = (29.2 - 2.76)\ \text{kJ} = 26.44\ \text{kJ}$$

Since work is done by the system, W is negative. ■

3.3 HEAT CHANGE AT CONSTANT VOLUME

If constant volume conditions are imposed, the mechanical work W would be zero and therefore Equation (3.5) gives

$$Q_V = U_2 - U_1 = \Delta U \tag{3.8}$$

where Q_V is the heat supplied to the system under constant volume.

3.4 RELATIONSHIP BETWEEN Q_P AND Q_V

From the definition of enthalpy, we get

$$H = U + PV \tag{3.9}$$

we can write, for constant pressure

$$\Delta H = \Delta U + P\Delta V \tag{3.10}$$

If the system consists of gases which are ideal ($PV = nRT$), using Equations (3.7) and (3.8) in Equation (3.10), we obtain

$$Q_P = Q_V + \Delta nRT \tag{3.11}$$

Equation (3.11) is quite useful particularly in the context of thermochemistry. One can compute the value of Q_P by knowing Q_V and vice versa. Illustrative examples on Equation (3.11) will be taken up when we come to thermochemistry.

EXAMPLE 3.4 For combustion of heptane C_7H_{16} in a constant volume calorimeter $Q_V = -4800$ kJ at 298 K, what is the change in enthalpy of the process at 298 K.

Solution We have the following chemical equation for combustion of heptane:

$$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(l)$$

From the definition of enthalpy

$$\Delta H = \Delta U + \Delta nRT$$

where

$$\Delta n = 7 - 11 = -4, \qquad T = 298\ \text{K}, \qquad R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$$

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Therefore,

$$\Delta H = Q_V + \Delta nRT$$
$$= -4800\,\text{kJ} + (-4)\,\text{mol} \times 8.314 \times 10^{-3}\,\text{kJK}^{-1}\,\text{mol}^{-1} \times 298\,\text{K}$$
$$= (-4800 - 9.91)\,\text{kJ}$$
$$= -4809.91\,\text{kJ} \quad \blacksquare$$

EXAMPLE 3.5 One mole of an ideal gas is expanded isothermally and reversibly at 25°C from a volume of 8.30 m^3 to 16.8 m^3. Calculate Q, W, ΔH.

Solution We have

$$PV = nRT, \quad \text{where} \quad n = 1$$
$$T_1 = 25 + 273 = 298\,\text{K}, \qquad T_2 = T_1 = 298\,\text{K}$$
$$V_1 = 8.30\,\text{m}^3, \qquad V_2 = 16.8\,\text{m}^3$$

Then

$$W = -\int_{V_1}^{V_2} P\,dV = -\int_{V_1}^{V_2} \frac{RT}{V}\,dV = -RT \ln \frac{V_2}{V_1}$$
$$= -2.303 \times 8.314\,\text{JK}^{-1}\,\text{mol}^{-1} \times 298\,\text{K} \times \log \frac{16.8\,\text{m}^3}{8.30\,\text{m}^3}$$
$$= -1747.3\,\text{J mol}^{-1}$$

We also have $\Delta U = U_2 - U_1$. In case of isothermal reversible expansion of an ideal gas $U_2 - U_1 = 0$. (For explanation see Section 3.5.) Therefore $\Delta U = 0$. Now, we obtain

$$Q + W = \Delta U = 0, \quad \text{then} \quad Q = -W = 1747.3\,\text{J mol}^{-1}$$

and

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(RT)$$

Since R and T are constants, $\Delta H = 0 + 0 = 0$. $\blacksquare$

3.5 HEAT CAPACITIES: C_P AND C_V

By definition, we have

$$C_P = \frac{(dQ)_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \tag{3.12}$$

and

$$C_V = \frac{(dQ)_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \tag{3.13}$$

As already discussed in Chapter 2, $C_P > C_V$. Now let us evaluate that how much larger is the value of C_P than the value of C_V. From Equations (3.12) and (3.13), we can write

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$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \tag{3.14}$$

Since $H = U + PV$,

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \tag{3.15}$$

Writing

$$U = U(V, T) = U(P, T) \tag{3.16}$$[1]

and

$$V = V(P, T) \tag{3.17}$$

We can write

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{3.18}$$

and

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \tag{3.19}$$

Therefore, from Equations (3.18) and (3.19)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT\right]$$

$$= \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T\right] dP \tag{3.20}$$

From Equation (3.16), since U can also be written as a function of P and T, the expression for dU can also be written as

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \tag{3.21}$$

Comparing the coefficients of dT and dP in Equations (3.20) and (3.21), we get

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{3.22}$$

and

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \tag{3.23}$$

---

1. The rationale behind Equations (3.16) and (3.17) will be dealt with in Chapter 4.

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In view of Equation (3.22), Equation (3.15) can be rewritten as

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{3.24}$$

Dimensional analysis will show that the term $\left(\partial U/\partial V\right)_T$ has dimensions of pressure ($Nm/m^3 = Nm^{-2}$). In fact, the term $\left(\partial U/\partial V\right)_T$ is called *internal pressure* and is a measure of internal cohesive forces of the gas. On a priori grounds therefore, it can be stated that for ideal gases $\left(\partial U/\partial V\right)_T = 0$, because no forces of attraction and repulsion are supposed to exist in an ideal gas. It is also consistent with the fact that KE of an ideal gas ($PV = nRT$) at constant temperature is constant. For n moles of an ideal gas ($PV = nRT$), therefore, it follows from Equation (3.24) that

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = nR \tag{3.25}$$

It is worth mentioning that historically, the conclusion $\left(\partial U/\partial V\right)_T = 0$ was arrived at by Joule through an experiment whose design was faulty. The experimental set-up used by Joule was of the type shown in Figure 3.3.

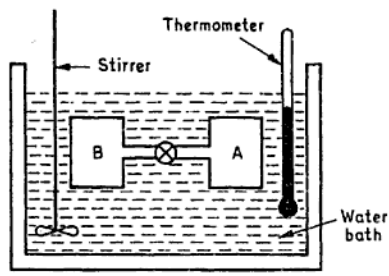

Figure 3.3 The Joule's experiment.

Bulb A was filled in with air and bulb B was evacuated; bulbs A and B were connected by a stopcock. The temperature of the surrounding water bath was noted. The stopcock was then opened and the temperature was again recorded. No change in temperature was observed as a result of this operation. Since the gas (air) expands into vacuum, no work is done either by the gas or on the gas. Further since no change in temperature was observed, the gas did not exchange any heat with the environment, otherwise temperature would have changed. Now invoking the first law of thermodynamics, we can write for this situation

$$dQ + dW = dU = 0 \tag{3.26}$$

(Since both dQ and dW are individually zero.) Also, since $U = U(V, T)$, we can write using Equation (3.26)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{3.27}$$

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Since $dT = 0$ as experimentally observed,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \neq 0 \quad \text{and} \quad dV \neq 0$$

there is no alternative to the conclusion that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{3.28}$$

This conclusion (Equation (3.28)) cannot be valid for air because its validity would imply that internal pressure which is a measure of attractive forces between molecules, is zero for air and we know for certain that air is not an ideal gas. However, the conclusion (3.28) is valid for ideal gases. In fact, the experimental design of Joule was at fault. Since heat capacity of the water calorimeter was extremely large in comparison to that of the gas used, Joule's experiment was not capable of detecting small temperature effects. Further verification of Equation (3.28) using thermodynamic equation of state will be taken up later, after we have dealt with the second law of thermodynamics. Expressions for the difference between C_P and C_V can be obtained in several alternative forms. Derivation of these equation is left to the student as an exercise.

EXAMPLE 3.6 What is the change in enthalpy when the temperature of 100 g of water is raised from 50°C to 100°C at constant pressure? Given C_P of water is 75.29 JK^{-1} mol^{-1}.

Solution From Equation (3.12), we have

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P, \qquad \text{therefore} \quad \Delta H = C_P \Delta T$$

When n moles of substance are in per cent, then

$$\Delta H = nC_P\Delta T = \frac{100\text{ g}}{18\text{ g/mol}} \times 75.29\text{ JK}^{-1}\text{mol}^{-1} \times 50\text{ K} = 20.91\text{ kJ} \quad \blacksquare$$

3.6 JOULE–THOMSON EXPERIMENT

The Joule–Thomson expansion, which essentially is adiabatic expansion, is one of the powerful methods for producing low temperatures. Schematic representations of the experimental set-up is shown in Figure 3.4.

This is quite a simple experiment in which a gas is forced passed through a porous plug from the high-pressure side (side A) to the low-pressure side (side B). The entire set-up (Figure 3.4) is thermally insulated so that adiabatic conditions prevail ($Q = 0$). The pressures on the sides A and B are maintained constant. In the left-hand side compartment A, work W_1 is done on the gas. Hence we can write

$$W_1 = P_1(V_1 - 0) = P_1V_1 \tag{3.29}$$

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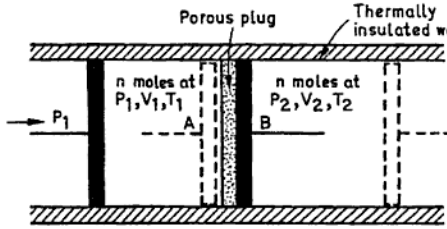

Figure 3.4 The Joule–Thomson experiment. The dotted lines indicate the final position of the piston.

Similarly, in the right-hand side compartment B, work W_2 is done by the gas on the piston and is given by

$$W_2 = P_2V_2 \tag{3.30}$$

Hence net work done on the gas would be given by

$$W = W_1 - W_2 = P_1V_1 - P_2V_2 \tag{3.31}$$

Since Q is zero (adiabatic condition) we can write from the first law, that is from Equations (3.1) and (3.31)

$$0 + P_1V_1 - P_2V_2 = U_2 - U_1 \tag{3.32}$$

or

$$U_1 + P_1V_1 = U_2 + P_2V_2$$

or

$$H_1 = H_2 \tag{3.33}$$

Thus, it follows that the Joule–Thomson expansion is an isoenthalpic process.

When the gas is forced passed through a porous plug from a higher pressure to a lower pressure the temperature in the compartment having lower pressure falls. The Joule–Thomson coefficient μ_{JT} is defined as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \approx \left(\frac{\Delta T}{\Delta P}\right)_H \tag{3.34}$$

It is obvious that positive values of μ_{JT} should correspond to cooling because in the experiment $\Delta P = P_2 - P_1 < 0$, hence $\Delta T = T_2 - T_1$ should also be negative, i.e. $T_2 < T_1$. Similarly the negative value of μ_{JT} corresponds to heating. When μ_{JT} is zero it indicates neither heating nor cooling. The temperature at which this happens is called *inversion temperature*. We will discuss inversion temperature in some detail in Chapter 5.

Writing H as a function of temperature and pressure, i.e.

$$H = H(T, P)$$

We can write

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{3.35}$$

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Since in the Joule–Thomson experiment $dH = 0$, it follows from Equation (3.35)

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \tag{3.36}$$

Also, since $H = U + PV$, Equation (3.36) can be rewritten as

$$\mu_{JT} = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

$$= -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right] \tag{3.37}$$

As already stated, $\left(\partial U/\partial V\right)_T$ has the dimensions of pressure, it is called *internal pressure* of the gas and is a measure of the attractive forces between the molecules of the gas. In the Joule–Thomson expansion, work is done against these attractive forces when the gas is forced through the pores of the porous plug. The gas gets wire-drawn and in this process loses its internal energy. This implies that the size of the pores of the porous plug should be of the order of mean free path of the gas so that only one molecule can pass at a time through the pores. In this process, molecules gets separated; the separation occurs against the attractive forces.

Let us now understand inversion temperature in the light of Equation (3.37). The term $\left(\partial U/\partial V\right)_T$, the internal pressure of the gas is approximately equal to a/V^2, a, being the constant occurring in the van der Waals equation[2] and is usually positive for real gases. Further, since it is approximately equal to a/V^2 it increases, with increasing pressure. The term $\left(\partial V/\partial P\right)_T$ in Equation (3.37) is always negative; volume decreases as pressure increases. An examination of the pressure–volume isotherms of gases would reveal that the numerical value of the slope $\left(\partial V/\partial P\right)$ is large at low pressure and diminishes as the pressure is increased. Thus, it follows that the first term in the square brackets on the right-hand side of Equation (3.37) is always negative. Now let us look at term $\left[\partial (PV)/\partial P\right]_T$ in Equation (3.37). At ordinary temperatures, this is negative for all gases except for hydrogen and helium at low pressure, but it becomes positive at high pressures. The behaviour of nitrogen is shown in Figure 3.5 as an example to help appreciate this point. At low and moderate pressures, therefore, both terms in the square bracket on the right-hand side of Equation (3.37) are negative. Since C_P is positive it follows that the Joule–Thomson coefficient μ_{JT} will have positive values. Let us now see what happens when the gas pressure is increased. Since the value of $\left(\partial U/\partial V\right)_T$ increases and the value of $\left(\partial V/\partial P\right)_T$ decreases as the pressure is increased, qualitatively it appears that the first term in the square brackets in Equation (3.37) would be more or less invariant with pressure. The second term

2. Your familiarity with the van der Walls equation is assumed.

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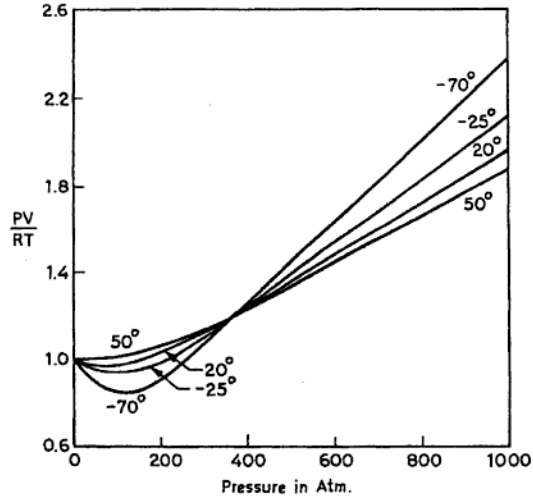

Figure 3.5 The *PV-P* behaviour of nitrogen.

in the square bracket would however decrease numerically and eventually becomes positive. Thus the value of the Joule–Thomson coefficient μ_{JT} should decrease with increasing pressure, pass through zero and finally change sign. At sufficiently high pressures, the coefficient μ_{JT} should become negative and produce a heating effect. At lower temperatures, not only is the numerical value of $\partial(PV)/\partial P$ larger at low pressure, but increased pressures must be attained before it changes sign. Therefore, at low pressure, the Joule–Thomson coefficient should increase as the temperature is diminished and higher pressures will be required before a reversal of sign occurs. The temperature at which the sign of μ_{JT} changes, at a given pressure, is called the *inversion temperature*. At the inversion temperature, of course, the value of μ_{JT} should be zero. It would also appear from these considerations that inversion temperature of any gas should increase with the pressure.

3.7 JOULE–THOMSON COEFFICIENT FOR AN IDEAL GAS

The Joule–Thomson coefficient is zero for an ideal gas is obvious from Equation (3.36). We also have

$$H = U + PV$$

For an ideal gas, U is a function of temperature only and $PV = nRT$. Thus

$$H = H(T) \tag{3.38}$$

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Therefore, it follows from Equation (3.38)

$$\mu_{JT} = 0$$

This means an ideal gas cannot be liquefied using Joule–Thomson expansion. Since all gases that we know so far have been liquefied, ideal gas does not exist except in our imagination. The fact that $\mu_{JT} = 0$, for an ideal gas can be seen to be consistent with the physical picture. An *ideal gas* is one, the molecules of which have no forces of attraction or repulsion amongst them. Therefore, when an ideal gas is forced through a porous plug no loss of internal energy takes place. In real gases, the molecules are separated against the force of attraction between them.

We will discuss the Joule–Thomson effect again after we complete dealing with the second law of thermodynamics. In the mean time, let us discuss heat changes during chemical and physico-chemical process (thermochemistry), which is an important implication of the first law of thermodynamics.

3.8 THERMOCHEMISTRY

Thermochemistry is the study of heat effects accompanying chemical reactions and changes like formation of solution and other changes in the state of matter like fusion, vaporization, sublimation and changes in the state of aggregation, etc. These heat effects are experimentally measured using calorimeters. The heat effects are measured either at constant pressure conditions or at constant volume conditions. For details of the experiments some standard text on thermochemical measurements should be consulted. Physico-chemical changes are categorized as 'exothermic' or 'endothermic' depending upon whether heat is evolved or absorbed by the system. The heat evolved by the exothermic processes is written with negative sign ($-\Delta H$) while in the case of endothermic process it is indicated by a positive sign ($+\Delta H$). This is consistent with the sign convention given in Chapter 2.

Now a few words about the terminology. The terminology is simple. The primary term is the *heat of the process*. When the process is a chemical reaction, it is known as *heat of reaction*, when it is formation reaction it is called *heat of formation* and so on. Thus the terms that are in use are, heat of reaction, heat of formation, heat of combustion, heat of solution, etc. The heat of reaction at constant pressure, in accordance with Equation (3.7) is written as

$$Q_P = \Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}} \tag{3.39}$$

and if the reaction is exothermic $\Sigma H_{\text{reactants}} > \Sigma H_{\text{products}}$ and reverse is the case if the reaction is endothermic, i.e. $\Sigma H_{\text{reactants}} < \Sigma H_{\text{products}}$. Similarly, if the heat of the reaction is measured under constant-volume conditions (bomb calorimeter), the heat of the reaction, in accordance with Equation (3.8) is given by

$$Q_V = \Delta U = \sum U_{\text{products}} - \sum U_{\text{reactants}} \tag{3.40}$$

Q_P and Q_V are related to each other, the relationship is given by Equation (3.11). This relationship is of utility in computing the value of Q_P from the knowledge of Q_V and vice versa. The following examples will illustrate the point.

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EXAMPLE 3.7 The heat of the reaction

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

is –97.03 KJ at 298 K, when measured in a bomb calorimeter. Compute the value of ΔH for this reaction.

Solution We have

$$\Delta U = 97030 \text{ Joules}$$

$$\Delta n = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

We also know that

$$\Delta H = \Delta U + \Delta nRT$$

$$= -97030 + \left(-\frac{1}{2}\right) (8.314) (298)$$

$$= -98270 \text{ J} \quad \blacksquare$$

EXAMPLE 3.8 From the following data:

(i) $C (s) + O_2 (g) = CO_2 (g)$; ΔH (298 K) = 393.5 kJ mol^{-1}

(ii) $C (s) + \frac{1}{2} O_2 = CO (g)$; ΔH (298 K) = –110.5 kJ mol^{-1}

Calculate the value of ΔU under the same conditions of temperature and pressure at which ΔH is reported.

Solution Use $\Delta H = \Delta U + \Delta nRT$. For reaction (i), $\Delta n = 1 - 1 = 0$; and for reaction (ii),

$$\Delta n = 1 - \frac{1}{2} = \frac{1}{2}$$

(see that in calculating Δn only gases are considered). Hence ΔU for reaction (i) = $-393.5 - 0 \times RT = -393.5$ kJ mol^{-1}, and ΔU for reaction (ii) = $-110.5 \times 1000 - 1/2 \times 8.314 \times 298 = -111.738$ kJ mol^{-1}. $\blacksquare$

3.9 THERMOCHEMICAL EQUATIONS

Thermochemical equations are balanced chemical equations written along with the energy change (ΔH or ΔU) associated with them. The state in which the reactants and the products exist is also indicated in the equation by indicating g, s and l for gaseous, solid and liquid states. For example, the equation

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$$CH_4\,(g) + 2O_2\,(g) = CO_2\,(g) + 2H_2O\,(l); \qquad \Delta H_{298\,K} = -890.3\ kJ$$

states that 1 mol of methane gas reacts (burns) with two moles of oxygen gas to give 1 mol of carbon dioxide gas and two moles of liquid water. In this process 890.3 kJ of heat is evolved which goes to the environment. Such reactions are commonly known as combustion reactions.

The standard change in enthalpy per mole of combustible substance is called *standard enthalpy of combustion* or *standard heat of combustion*, $\Delta H^\circ_{combustion}$.

Examples of some combustion reactions and $\Delta H^\circ_{combustion}$ values are shown in Table 3.1.

Table 3.1 Combustion Reactions and Their $\Delta H^\circ_{combustion}$/kJ mol^{-1}

Substance	Combustion equation	$\Delta H^\circ_{combustion}$/kJ mol^{-1}
Methanol	$2CH_3OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 4H_2O\,(l)$	–726
Glucose	$C_6H_{12}O_6\,(s) + 6O_2\,(g) \rightarrow 6CO_2\,(g) + 6H_2O\,(l)$	–2808
Hydrogen	$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$	–286
Benzene	$2C_6H_6\,(l) + 15O_2\,(g) \rightarrow 12CO_2\,(g) + 6H_2O\,(l)$	–3268

EXAMPLE 3.9 The standard heat of reaction

$$2C_6H_6\,(l) + 15O_2\,(g) \rightarrow 12CO_2\,(g) + 6H_2O\,(l)$$

is $\Delta H^\circ = -6536$ kJ mol^{-1}. What is the value of standard heat of combustion of the above reaction?

Solution The reaction of combustion of 1 mol of C_6H_6 is

$$C_6H_6\,(l) + \frac{15}{2}O_2\,(g) \rightarrow 6CO_2\,(g) + 3H_2O\,(l)$$

Therefore,

$$\Delta H^\circ = -\frac{6536}{2} = -3268\ kJ\ mol^{-1}$$

Thus, the standard heat of combustion = $\Delta H^\circ_{combustion} = -3268$ kJ mol^{-1} ■

3.10 HEAT OF FORMATION

The heat of formation of a compound is the change in heat content ΔH when one mole of the substance is formed from its elements, at a given temperature and pressure. In computing heat of reactions in general and heats of formation in particular it is convenient to talk of reaction heats at the standard state. The convention is that the heat of formation of elements in their standard states is zero. The meanings of standard states for various forms of matter are given below:

Gas: Ideal gas at 1 atmosphere and the given temperature

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Liquid: Pure liquid at 1 atmosphere and the given temperature

Solid: Stable crystalline form at 1 atmosphere and given temperature, e.g. graphite, rhombic sulphur, etc.

The reaction heats at standard states are symbolically written as ΔU° and ΔH°. In the following thermo-chemical equation for the formation reaction of CO_2

$$C(s) + O_2(g) = CO_2(g); \qquad \Delta H^\circ_{298\,K} = -393.5 \text{ kJ mol}^{-1}$$

carbon is in the form of graphite, for this is the stable form, i.e. standard state at 25°C and 1 atmosphere pressure; the gases, oxygen and carbon dioxide are both at 1 atmosphere pressure. The standard heat of formation of carbon dioxide at 25°C is then said to be -393.5 kJ mol^{-1} which means that the heat content of one mole of carbon dioxide is less than that of 1-g atom of graphite and 1 mole of oxygen by 393.5 kJ at 25°C and 1 atmosphere pressure.

With these considerations the useful connection between the standard heats of formation of the reactants and products and the standard heat of reaction becomes obvious. Since conventionally heats of formation of elements in their standard states are zero, it is obvious that standard heat of formation of a compound is nothing but its enthalpy or heat content (H) at the standard state. It is therefore easy to see that heat of any reaction at standard state can be computed from the standard heat of formation data for reactants and the products. For example, consider the reaction:

$$\begin{aligned} &CH_4 + 2O_2(g) = CO_2(g) + 2H_2O(l) \\ &-17.89 \quad 2\times 0 \qquad -94.05 - 2\times 68.32 \end{aligned}$$

at 25°C. The standard heats of formation (kcals) at 25°C of each reactant and product species have been written below. It is now easy to compute the standard heat of the above reaction

$$\Delta H^\circ_{298K} = \left[(-94.05) + (-2\times 68.32) - (-17.89) - 2\times 0\right] = 212.80 \text{ kcal}$$

It should also be obvious that the heat of dissociation of a compound should be equal to its heat of formation in magnitude but opposite in sign. For example, if

$$H_2 + \frac{1}{2}O_2(g) = H_2O(l) \qquad \Delta H_{298K} = -285.830 \text{ kJ}$$

then

$$H_2O(l) = H_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H_{298K} = +285.830 \text{ kJ}$$

The standard heat of formation of some substances at 25°C is shown in Table 3.2.

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Table 3.2 Standard Heat of Formation

Substance	ΔH_f°/kJ mol^{-1}
Ammonia, NH_3 (g)	−46.11
Carbon monoxide, CO (g)	−110.53
Carbon dioxide, CO_2 (g)	−393.51
Hydrogen chloride, HCl (g)	−92.31
Hydrogen sulphide, H_2S (g)	−20.63
Nitrogen oxide, N_2O (g)	+82.05
Sulphuric acid, H_2SO_4 (l)	−813.99
Water vapour, H_2O (g)	−241.82
Water, H_2O (l)	−285.83
Benzene, C_6H_6 (l)	+49.00
Methanol, CH_3OH (l)	−238.66
Glucose, $C_6H_{12}O_6$ (s)	−1274.00
Sucrose, $C_{12}H_{22}O_{11}$ (s)	−2222.00
Urea, $CO(NH_2)_2$ (s)	−333.51
Oxalic acid, $(COOH)_2$ (s)	−82.20

EXAMPLE 3.10 The standard heat of reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

is $\Delta H^\circ = -92.22$ kJ mol^{-1}. What is the standard heat of formation of NH_3 (g).

Solution The equation of formation of 1 mol of NH_3 (g) is

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$

Therefore,

$$\Delta H^\circ = \Delta H_f^\circ = -\frac{92.22}{2} = -46.11 \text{ kJ mol}^{-1} \quad \blacksquare$$

EXAMPLE 3.11 The standard heats of formation of liquid water, liquid ethanol and carbon dioxide gas at 25°C are −285.83, −277.69 and −393.51 kJ/mol. Find out the standard heat of following reaction at 25°C:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Solution We have

$$\Delta H^\circ_{298\,K} = 2\Delta H_f^\circ(CO_2, g) + 3 \times \Delta H_f^\circ(H_2O, l) - \left[\Delta H_f^\circ(C_2H_5OH, l) + 3\Delta H_f^\circ(O_2, g)\right]$$

$$= 2 \times (-393.51) + 3(-285.83) - [(-277.69) + 3 \times 0)]$$

$$= (-787.02 - 857.49) - (-277.69)$$

$$= -1644.51 + 277.69$$

$$= -1366.82 \text{ kJ} \quad \blacksquare$$

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3.11 THERMOCHEMICAL IMPLICATION OF THE FIRST LAW

Since both U and H are state functions, i.e. dU and dH are exact differentials, it follows that heat of a reaction under a given set of conditions (e.g. temperature, pressure, etc.) should be independent of its mechanism. The mechanism of a reaction, in fact, is the path between the initial and the final states. This abstraction is from the well-known law of constant heat summation first stated empirically by G.H. Hess, as early as 1840. This law states that "the resultant heat change at constant pressure or constant volume in a given chemical reaction is the same whether it takes place in one or several stages". Suppose there are two ways of conducting a chemical reaction:

(a) $A \rightarrow D$ and
(b) (i) $A \rightarrow B$, (ii) $B \rightarrow C$, (iii) $C \rightarrow D$

In the mechanism (a) the heat of reaction at constant pressure ΔH would be given by

$$\Delta H = H_D - H_A \tag{3.41}$$

In the mechanism (b), the heats of reactions of the steps (i), (ii) and (iii) would be respectively given by

$$\Delta H_1 = H_B - H_A, \qquad \Delta H_2 = H_C - H_B, \qquad \Delta H_3 = H_D - H_C \tag{3.42}$$

It is clear from Equations (3.41) and (3.42) that

$$\Delta H = H_D - H_A = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{3.43}$$

Similar considerations would apply for reaction heats at constant volume. Thus, it would appear that the Hess's law of constant heat summation is just the first law (the law of energy conservation) stated in the thermochemical context.

From a functional point of view one should remember the following two rules for thermochemical calculations:

1. Chemical equations can be reversed and when it is done the sign of ΔH is changed. That is if $A + B \rightarrow C$; $\Delta H = Q$ Joules, then for $C \rightarrow A + B$; $\Delta H = -Q$ Joules.
2. Thermochemical equation in many respects can be treated like algebraic equations. Thermochemical equations can be added, subtracted or multiplied and divided by an integer etc.

The following example would illustrate the use of these rules in thermochemical computations.

EXAMPLE 3.12 The standard heat of reaction

$$\mathrm{CO\,(g) + NO\,(g) \rightarrow \frac{1}{2}N_2(g) + CO_2(g)}$$

is -374 J at 25°C. If the standard heat of formation of NO (g) and CO_2 (g) are $+90.25$ kJ mol^{-1} and -393.51 kJ mol^{-1}, then what is the value of standard heat of formation of CO (g).

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Solution Given that, $\Delta H^\circ_{298K} = -374$ kJ. Here

$$\Delta H^\circ_{298K} = \frac{1}{2}\Delta H^\circ_f(N_2, g) + \Delta H^\circ_f(CO_2, g) - \left[\Delta H^\circ_f(CO, g) + \Delta H^\circ_f(NO, g)\right]$$

$$-374 = \frac{1}{2}\times 0 + (-393.51) - \Delta H^\circ_f(CO, g) - 90.25$$

Then

$$\Delta H^\circ_f(CO, g) = +374 - 393.51 - 90.25$$
$$= 374 - 483.76$$
$$= -109.76 \text{ kJ mol}^{-1} \quad \blacksquare$$

EXAMPLE 3.13 The standard heat of hydrogenation of gaseous propylene to propane is –29.6 kcal and the heat of combustion of propane is –530.6 kcal at 25°C. Assume constant pressure conditions. If the heats of formation of carbon dioxide is –294.0 kcal and of liquid water –68.3 kcal. Calculate the heat of combustion and the standard heat of formation of propylene.

Solution The given data can be written as

$$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g);\ \Delta H^\circ = -29.6 \text{ kcal} \quad (1)$$

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(1);\ \Delta H^\circ = -530.6 \text{ kcal} \quad (2)$$

$$C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H^\circ = -94.0 \text{ kcal} \quad (3)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1);\ \Delta H^\circ = -68.3 \text{ kcal} \quad (4)$$

We have to find out the heat of combustion of propylene, i.e. heat of the reaction

$$C_3H_6(g) + 4\frac{1}{2}\ O_2(g) \rightarrow 3CO_2(g) + 3H_2O(1) \quad (5)$$

and the heat of formation of propylene, i.e. heat of the reaction

$$3C(s) + 3H_2(g) \rightarrow C_3H_6(g) \quad (6)$$

Using the data given by the equations (1) to (4), the heat of reaction (6) can be obtained by adding equations (1) and (2) and then subtract the sum from 3 times equations (3) and 4 times equation (4). Thus ΔH° for equation (6) would be

$$\Delta H^\circ = [3(-94.0) + 4(-68.3)] - [(-29.6) + (-530.6)] = 5.0 \text{ kcal}$$

Similarly to find the value of ΔH° for equation (5), reverse equation (6) and add to it 3 times equations (3) and (4). Thus ΔH° for equation (5) would be

$$\Delta H^\circ = -5 + 3(-94.0) + 3 \times (-68.3) = -491.9 \text{ kcal} \quad \blacksquare$$

EXAMPLE 3.14 From the following data calculate the standard heat of formation of N_2O_5 (g):

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g);\ \Delta H^\circ = -114.1 \text{ kJ mol}^{-1} \quad (1)$$

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$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g);\ \Delta H^\circ = -110.2 \text{ kJ mol}^{-1} \quad (2)$$

$$N_2(g) + O_2(g) \rightarrow 2NO(g);\ \Delta H^\circ = +180.5 \text{ kJ mol}^{-1} \quad (3)$$

Solution Reaction of formation of 2 moles of N_2O_5 (g) from its elements is

$$2N_2(g) + 5O_2(g) \rightarrow 2N_2O_5(g),\ \Delta H_f^\circ = ?$$

Multiplying Equation (1) by 2, we get

$$4NO(g) + 2O_2(g) \rightarrow 4NO_2(g) \quad (4)$$

where

$$\Delta H^\circ = 2 \times (-114.1) = -228.2 \text{ kJ mol}^{-1}$$

Equation (3) multiplied by 2 gives

$$2N_2(g) + 2O_2(g) \rightarrow 4NO(g) \quad (5)$$

where $\Delta H^\circ = 2 \times 180.5 \text{ kJ mol}^{-1} = 361.0 \text{ kJ mol}^{-1}$. Adding equations (2), (4) and (5), we get

$$2N_2(g) + 5O_2(g) \rightarrow 2N_2O_5(g) \quad (6)$$

where

$$\Delta H^\circ = (-110.2 - 228.2 + 361.0) \text{ kJ mol}^{-1} = 22.6 \text{ kJ mol}^{-1}$$

Equation (6) is the reaction of formation of N_2O_5 from its elements. Therefore, heat change for the formation of 2 moles of N_2O_5 (g) = 22.6 kJ mol^{-1}. Thus

$$\text{standard heat of formation of } N_2O_5(g) = \frac{22.6}{2} = 11.3 \text{ kJ mol}^{-1} \quad \blacksquare$$

EXAMPLE 3.15 Calculate the standard heat of formation of solid sucrose if the standard enthalpy of combustion of solid sucrose is –5645 kJ mol^{-1} and standard heat of formation of CO_2 (g) and H_2O (l) are –393.51 and –285.83 kJ mol^{-1} respectively.

Solution Combustion of solid sucrose is shown in the following equation:

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l);\ \Delta H^\circ_{\text{combustion}} = -5645 \text{ kJ mol}^{-1} \quad (1)$$

We can also write,

$$C(s) + O_2(g) \rightarrow CO_2(g);\ \Delta H^\circ_f = -393.5 \text{ kJ mol}^{-1} \quad (2)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta H^\circ_f = -285.83 \text{ kJ mol}^{-1} \quad (3)$$

$$12CO_2(g) + 11H_2O(l) \rightarrow C_{12}H_{22}O_{11}(s) + 12O_2(g);\ \Delta H_1 = 5645 \text{ kJ mol}^{-1} \quad (4)$$

$$12C(s) + 12O_2(g) \rightarrow 12CO_2(g);\ \Delta H_2 = 12 \times (-393.5) = -4722 \text{ kJ mol}^{-1} \quad (5)$$

$$11H_2(g) + \frac{11}{2}O_2(g) \rightarrow 11H_2O(g);\ \Delta H_3 = 11 \times (-285.83) = -3144.13 \text{ kJ mol}^{-1} \quad (6)$$

Adding equations (4), (5) and (6), we get

$$12C(s) + 11H_2(g) + \frac{11}{2}O_2(g) \rightarrow C_{12}H_{22}O_{11}(s)$$

Therefore,

$$\Delta H^\circ = \Delta H^\circ_f = (5645 - 4722 - 3144.13) \text{ kJ mol}^{-1} = -2221.13 \text{ kJ mol}^{-1} \quad \blacksquare$$

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3.12 VARIATION OF REACTION HEATS WITH TEMPERATURE

It is often required to calculate the heat of reaction at a certain temperature from the knowledge of its value at some other temperature. This can be achieved using Kirchhoff equation derived below. Consider the generalized reaction

$$aA + bB + \cdots = lL + mM + \cdots$$

where capital letters indicate the reactant and the product species and the small letters are stoichiometric numbers. ΔH for this reaction would be given by the equation

$$\Delta H = (lH_L + mH_M + \cdots) - (aH_A + bH_B + \cdots) \tag{3.44}$$

Differentiating Equation (3.44) with respect to temperature holding pressure constant, we get

$$\left[\frac{\partial \Delta H}{\partial T}\right]_P = \left[l\left(\frac{\partial H_L}{\partial T}\right)_P + m\left(\frac{\partial H_M}{\partial T}\right)_P + \cdots\right] - \left[a\left(\frac{\partial H_A}{\partial T}\right)_P + b\left(\frac{\partial H_B}{\partial T}\right)_P + \cdots\right] \tag{3.45}$$

Remembering that $\left(\partial H/\partial T\right)_P = C_P$, Equation (3.45) can be rewritten as

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \sum\left(nC_P\right)_{\text{products}} - \sum\left(nC_P\right)_{\text{reactants}} = \Delta C_P \tag{3.46}$$

From Equation (3.46), it follows that

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT \tag{3.47}$$

ΔH_1 and ΔH_2 are the reaction heats at temperatures T_1 and T_2. Equations (3.46) and (3.47) are the forms of well-known Kirchhoff equation. If T_1 and T_2 are not too far apart C_P and hence ΔC_P can be taken to be invariant with temperature, we get from Equation (3.47)

$$\Delta H_2 - \Delta H_1 = \Delta C_P\left(T_2 - T_1\right) \tag{3.48}$$

If, however, T_1 and T_2 are too far apart and ΔC_P cannot be taken to be invariant with temperature, there are two ways of solving Equation (3.47). Either ΔC_P is taken as the mean value $\Delta \bar{C}_P$ in the temperature range from T_1 to T_2 or the variation of C_P with temperature is taken into account. In the first case Equation (3.48) would read as

$$\Delta H_2 - \Delta H_1 = \Delta \bar{C}_P\left(T_2 - T_1\right) \tag{3.49}$$

In the case of the second alternatives, C_P is written as a function of temperature in the form of a power series, i.e.

$$C_P = \alpha + \beta T + \gamma T^2 + \cdots \tag{3.50}$$

where α, β, γ, etc. are constants. In view of Equation (3.50), ΔC_P can be written as

$$\Delta C_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \cdots \tag{3.51}$$

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where

$$\Delta\alpha = (1\alpha_L + m\alpha_M + \cdots) - (a\alpha_A + b\alpha_B + \cdots)$$
$$\Delta\beta = (1\beta_L + m\beta_M + \cdots) - (a\beta_A + b\beta_B + \cdots) \quad (3.52)$$
$$\Delta\gamma = (1\gamma_L + m\gamma_M + \cdots) - (a\gamma_A + b\gamma_B + \cdots)$$

Utilizing Equation (3.51) and integrating Equation (3.47), we get

$$\Delta H_2 - \Delta H_1 = \Delta\alpha(T_2 - T_1) + \frac{1}{2}\Delta\beta\left(T_2^2 - T_1^2\right) + \frac{1}{3}\Delta\gamma\left(T_2^3 - T_1^3\right) + \cdots \quad (3.53)$$

Equation (3.53) can be used to calculate the heat of reaction at any temperature provided its value at one temperature is known. Similarly for the heat of reaction at constant volume, the Kirchhoff equation can be derived as

$$\left[\frac{\partial \Delta U}{\partial T}\right]_V = \Delta C_V \quad (3.54)$$

Its integration yields the equation

$$\Delta U_2 - \Delta U_1 = \Delta C_V(T_2 - T_1) \quad (3.55)$$

which is similar to the Equation (3.48).

EXAMPLE 3.16 The standard heat of formation of NH_3 (g) at 25°C is –46.11 kJ mol^{-1}. What is the standard heat of formation of NH_3 (g) at 127°C if the values of molar heat capacities at constant pressure of N_2 (g), H_2 (g) and NH_3 (g) are 29.125 JK^{-1} mol^{-1}, 28.824 JK^{-1} mol^{-1} and 35.06 JK^{-1} mol^{-1}, respectively. Consider that C_P is invariant with temperature.

Solution We have from the problem

$$T_1 = 25 + 273 = 298 \text{ K} \quad \text{and} \quad T_2 = 127 + 273 = 400 \text{ K}$$

Then

$$\Delta H^\circ_{400\text{K}} - \Delta H^\circ_{298\text{K}} = \int_{T_1}^{T_2} \Delta C_P \Delta T = \Delta C_P(T_2 - T_1)$$

We also have

$$\frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g) \rightarrow NH_3\,(g)$$

Then

$$\Delta C_P = C_P(NH_3, g) - \left[\frac{1}{2}C_P(N_2, g) + \frac{3}{2}C_P(H_2, g)\right]$$

$$= \left(35.06 - \frac{1}{2} \times 29.125 - \frac{3}{2} \times 28.824\right) JK^{-1}\ mol^{-1}$$

$$= (35.06 - 14.5625 - 43.236)\ JK^{-1}\ mol^{-1}$$

$$= -22.74\ JK^{-1}\ mol^{-1}$$

$$= -22.74 \times 10^{-3}\ kJK^{-1}\ mol^{-1}$$

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Therefore,

$$\Delta H^{\circ}_{400K} = -46.11 \text{ kJ mol}^{-1} - [22.74 \times 10^{-3} \text{ kJK}^{-1} \text{ mol}^{-1} \times (400 - 298) \text{ K}]$$
$$= -46.11 \text{ kJ mol}^{-1} - 2.3195 \text{ kJ mol}^{-1}$$
$$= -48.429 \text{ kJ mol}^{-1} \quad \blacksquare$$

EXAMPLE 3.17 The standard heat of formation of H_2O (g) at 25°C is –241.82 kJ mol^{-1}. What is the heat of formation of H_2O (g) at 1000°C? Given

$$C_P(H_2, g) = 29.07 - 0.836 \times 10^{-3}T + 20.1 \times 10^{-7}T^2$$
$$C_P(O_2, g) = 25.72 + 12.98 \times 10^{-3}T - 38.6 \times 10^{-7}T^2$$
$$C_P(H_2O, g) = 30.36 + 9.61 \times 10^{-3}T + 11.8 \times 10^{-7}T^2$$

Solution Since

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

We have

$$\Delta C_P(H_2O, g) = C_P(H_2O, g) - \left[C_P(H_2, g) + \frac{1}{2}C_P(O_2, g)\right]$$
$$= 30.36 + 9.61 \times 10^{-3}T + 11.8 \times 10^{-7}T^2 - 29.07 + 0.836 \times 10^{-3}T$$
$$- 20.1 \times 10^{-7}T^2 - \frac{1}{2} \times 25.72 - \frac{1}{2} \times 12.98 \times 10^{-3}T$$
$$+ \frac{1}{2} \times 38.6 \times 10^{-7}T^2$$
$$= -11.57 + 3.956 \times 10^{-3}T + 1.1 \times 10^{-6}T^2$$

Therefore,

$$\Delta H^{\circ}_{1273K} - \Delta H^{\circ}_{298K} = \int_{298}^{1273} \Delta C_P \Delta T$$
$$= \int_{298}^{1273} \left(-11.57 + 3.956 \times 10^{-3}T + 1.1 \times 10^{-6}T^2\right) \Delta T$$
$$= \left[-11.57T\right]_{298}^{1273} + \left[3.956 \times 10^{-3} \times \frac{1}{2} \times T^2\right]_{298}^{1273}$$
$$+ \left[\frac{1}{3} \times 1.1 \times 10^{-6}T^3\right]_{298}^{1273}$$

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$$= -11.57\,(1273 - 298) + 1.978 \times 10^{-3}\left(1273^2 - 298^2\right)$$
$$+ 0.37 \times 10^{-6}\left(1273^3 - 298^3\right)$$
$$= -11280.75 + 3029.8 + 753.49$$
$$= -7497.46 \text{ J mol}^{-1}$$

Thus

$$\Delta H^\circ_{1273K} = \Delta H^\circ_{298K} - 7497.46 \text{ J mol}^{-1}$$
$$= -241.82 \times 10^3 \text{ J mol}^{-1} - 7497.45 \text{ J mol}^{-1}$$
$$= -248.5 \text{ kJ mol}^{-1} \quad \blacksquare$$

3.13 APPLICATIONS OF THERMOCHEMICAL DATA

Thermochemical data are helpful in deciphering the mechanisms of many chemical, physical, physico-chemical and biological processes and have several applications. Here we will briefly discuss two representative applications. These are: (i) calculating the chemical bond energy and (ii) calculating the maximum flame temperature in ignition reactions.

Chemical bond energy

Let us take the methane molecule as an example. It has four C–H bonds which are equivalent. Therefore the C–H bond energy would be equal to $\frac{1}{4}\Delta H^\circ$ of the reaction:

$$CH_4\,(g) \rightarrow C\,(g) + 4H\,(g)$$

For this reaction, ΔH° can be calculated from the following data:

(i) $C\,(\text{graphite}) \xrightarrow{\text{Sublimation}} C\,(g), \quad \Delta H^\circ = 716.68 \text{ kJ}$

(ii) $\frac{1}{2}H_2\,(g) \xrightarrow{\text{Dissociation}} H(g), \quad \Delta H^\circ = 217.97 \text{ kJ}$

(iii) $C\,(\text{graphite}) + 2H_2\,(g) \rightarrow CH_4\,(g), \quad \Delta H^\circ = -74.75 \text{ kJ}$

Now multiplying equation (ii) by 4 and reversing equation (iii) and combining these two equations with equation (i), we get

$$2H_2\,(g) \rightarrow 4H\,(g);\ \Delta H^\circ = 871.88 \text{ kJ}$$
$$CH_4\,(g) \rightarrow C\,(\text{graphite}) + 2H_2\,(g);\ \Delta H^\circ = +74.75 \text{ kJ}$$
$$C\,(\text{graphite}) \rightarrow C\,(g);\ \Delta H^\circ = 716.68 \text{ kJ}$$

Adding, we get

$$CH_4\,(g) \rightarrow C\,(g) + 4H;\ \Delta H^\circ = 1663.31 \text{ kJ}$$

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Thus

$$\text{C–H bond energy in methane} = \frac{1663.31}{4}\ \text{kJ} = 415.82\ \text{kJ}$$

The value thus computed is very close to the actual value, 413 kJ.

EXAMPLE 3.18 Calculate the C–H bond energy of CH_4 from the following bond dissociation energy

$$CH_4 \rightarrow CH_3 + H; \quad \Delta H_1^\circ = 435\ \text{kJ mol}^{-1} \tag{1}$$

$$CH_3 \rightarrow CH_2 + H; \quad \Delta H_2^\circ = 364\ \text{kJ mol}^{-1} \tag{2}$$

$$CH_2 \rightarrow CH + H; \quad \Delta H_3^\circ = 385\ \text{kJ mol}^{-1} \tag{3}$$

$$CH \rightarrow C + H; \quad \Delta H_4^\circ = 335\ \text{kJ mol}^{-1} \tag{4}$$

Solution The bond dissociation energy for a particular bond depends on residual part of the molecule. The C–H bond energy in CH_4 and CH_3 are not same. Therefore the bond energy for a particular bond is mean bond dissociation energy. Here

$$\text{C–H bond energy} = \frac{435 + 364 + 385 + 335}{4}\ \text{kJ mol}^{-1} = 379.8\ \text{kJ mol}^{-1} \quad \blacksquare$$

EXAMPLE 3.19 Calculate the C–C bond energy in ethane using the given data:

$$2C\,(s) + 3H_2\,(g) \rightarrow C_2H_6\,(g); \quad \Delta H = -84.68\ \text{kJ mol}^{-1} \tag{1}$$

$$2C\,(s) \rightarrow 2C\,(g); \quad \Delta H = 2 \times 716.68\ \text{kJ} \tag{2}$$

$$3H_2\,(g) \rightarrow 6H\,(g); \quad \Delta H = 3 \times 436\ \text{kJ} \tag{3}$$

Solution Reversing equation (1), we get

$$C_2H_6\,(g) \rightarrow 2C\,(s) + 3H_2\,(g); \quad \Delta H_1 = 84.68\ \text{kJ mol}^{-1} \tag{4}$$

$$2C\,(s) \rightarrow 2C\,(g); \quad \Delta H_2 = 1433.36\ \text{kJ} \tag{2}$$

$$3H_2\,(g) \rightarrow 6H\,(g); \quad \Delta H_3 = 1308\ \text{kJ} \tag{3}$$

Adding (2), (3) and (4), we get

$$C_2H_6\,(g) \rightarrow 2C\,(g) + 6H\,(g); \quad \Delta H = 2826.04\ \text{kJ mol}^{-1}$$

Therefore, bond energy for breaking one C–C bond and six C–H bond is 2826.04 kJ mol^{-1}. Taking bond energy for one C–H bond $\approx$ 412 kJ mol^{-1}, we have

$$\text{Bond energy for 6 C–H bond} = 6 \times 412 = 2472\ \text{kJ mol}^{-1}$$

Therefore,

$$\text{Bond energy for one C–C bond in ethane bond} = (2826.04 - 2472)\ \text{kJ} = 354.04\ \text{kJ mol}^{-1}$$

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3.14 LATTICE ENTHALPY

Lattice enthalpy is the molar enthalpy change for the complete separation of constituent ions in case of ionic solids or constituent molecules in case of molecular solids under standard conditions. It is written as ΔH_L°. For example, molar enthalpy change for the complete separation of NaCl solid into its constituent ions Na^+ (g) and Cl^-(g) is 786 kJ.

Therefore, lattice enthalpy of NaCl is 786 kJ mol^{-1}.

$$NaCl\,(s) \rightarrow Na^+\,(g) + Cl^-\,(g); \qquad \Delta H_L^\circ = 786\ kJ\ mol^{-1}$$

In case of

$$Na^+\,(g) + Cl^-\,(g) \rightarrow NaCl\,(s); \qquad \Delta H^\circ = -786\ kJ\ mol^{-1}$$

Lattice enthalpy can be determined experimentally by Born–Haber cycle. This cycle is built up by the different steps of formation of lattice, where each step is accompanied by an enthalpy change. Since it is a cyclic process, the sum of enthalpy changes of all steps is equal to zero because of the fact that enthalpy is a state property.

Following are different steps of formation of NaCl crystal and corresponding values of enthalpy changes.

1. Sublimation or atomization of solid sodium:

$$Na\,(s) \rightarrow Na\,(g); \qquad \Delta H_1^\circ = 107.32\ kJ\ mol^{-1}$$

2. Formation of chlorine atoms by the dissociation of chlorine molecules:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl\,(g); \qquad \Delta H_2^\circ = 122\ kJ\ mol^{-1}$$

3. Formation of sodium ions by the ionization of gaseous sodium atoms:

$$Na\,(g) \rightarrow Na^+\,(g) + e\,(g); \qquad \Delta H_3^\circ = 494\ kJ\ mol^{-1}$$

4. Formation of chloride ions from chlorine atoms:

$$Cl\,(g) + e\,(g) \rightarrow Cl^-\,(g); \qquad \Delta H_4^\circ = -349\ kJ\ mol^{-1}$$

5. Formation of sodium chloride lattice or solid sodium chloride by the combination of gaseous sodium ions and chloride ions:

$$Na^+\,(g) + Cl^-\,(g) \rightarrow NaCl\,(s); \qquad -\Delta H_L^\circ = ?$$

Now to complete the cycle we have to consider the dissociation of NaCl (s) into Na (s) and $\frac{1}{2}Cl_2$ (g), i.e. the reverse of the formation of NaCl (s) from its elements.

6. Therefore,

$$NaCl\,(s) \rightarrow Na\,(s) + \frac{1}{2}Cl_2(g); \qquad \Delta H_5^\circ = 411.15\ kJ\ mol^{-1}$$

Now, the complete cycle is as follows:

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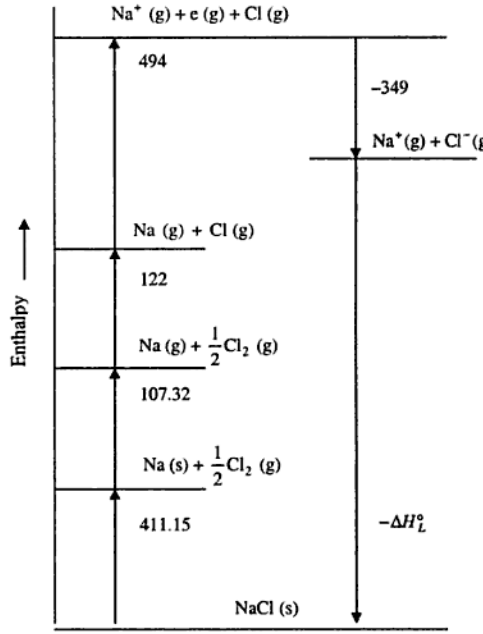

Hence

$$\Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ - \Delta H_L^\circ + \Delta H_5^\circ = 0$$

or

$$\left(107.32 + 122 + 494 - 349 - \Delta H_L^\circ + 411.15\right) \text{ kJ mol}^{-1} = 0$$

Therefore,

$$\Delta H_L^\circ = +785.47 \text{ kJ mol}^{-1}; \quad \text{lattice enthalpy } \Delta H_L^\circ = 785.47 \text{ kJ mol}^{-1}$$

EXAMPLE 3.20 Calculate the lattice enthalpy of magnesium bromide using the following data and draw the Born–Haber cycle:

Enthalpy of sublimation of Mg (s) = 148 kJ mol^{-1}
Enthalpy of ionization of Mg (g) to Mg^{+2} (g) = +2187 kJ mol^{-1}
Enthalpy of vaporization of Br_2 (l) = +31 kJ mol^{-1}
Enthalpy of dissociation of Br_2 (g) to 2Br (g) = 193 kJ mol^{-1}
Enthalpy of formation of Br^- (g) = −325 kJ mol^{-1}
Enthalpy of formation of $MgBr_2$ (s) from its element = −524 kJ mol^{-1}

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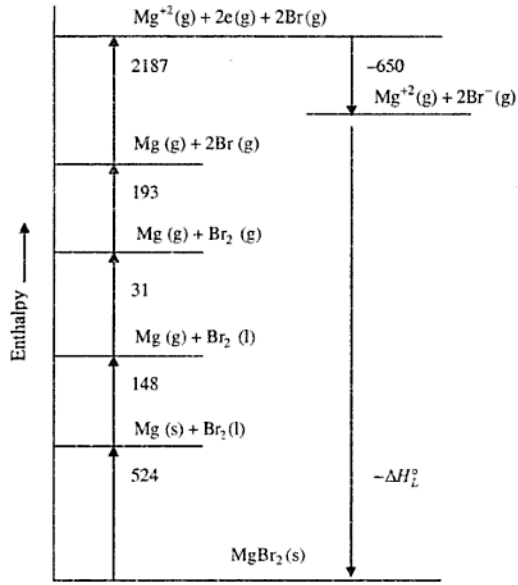
Solution



Therefore,

$$\left(524 + 148 + 31 + 193 + 2187 - 650 - \Delta H_L^\circ\right) \text{kJ mol}^{-1} = 0$$

or

$$\Delta H_L^\circ = +2433 \text{ kJ mol}^{-1}$$

Enthalpy change accompanying the reaction

$$MgBr_2 (s) \rightarrow Mg^{+2} (g) + 2Br^- (g)$$

is the lattice enthalpy. Thus $\Delta H_L^\circ = +2433$ kJ mol^{-1}. ■

3.15 FLAME AND EXPLOSION TEMPERATURE

In the discussion so far it has been implied that isothermal conditions prevail and the heat evolved or absorbed is removed or supplied by the environment. It is this heat which has been termed as heat of the reaction.

However, if adiabatic conditions prevail, in the case of exothermic reactions the heat liberated will be utilized to heat the products formed and the temperature of the reaction system would rise. In the case of endothermic reactions the temperature of the reaction system would fall. If the reaction is performed under constant pressure conditions, in the case of exothermic reactions the products may be heated up to sufficient temperatures to produce a flame and in that case it is

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called the maximum flame temperature or calorific intensity. If the reaction is performed under constant volume conditions, the quantity of heat liberated would be ΔU and the temperature in this case would be called 'explosion temperature'. The principle involved in the calculation of maximum temperatures is simple—heat evolved in the reaction goes to heat the products and whatever species are present finally. The following example may clarify the principle involved in the calculations.

EXAMPLE 3.21 The heat of combustion of methane is –881.25 kJ mol^{-1} at 298 K and the heat of vaporization of water at 298 K is 43.60 kJ mol^{-1}. What would be the maximum flame temperature when one mole of methane is burnt completely in calculated amount of air (N_2 to O_2 ratio 4), at constant pressure. The heat capacities of the various species and their temperature dependence are as follows:

$$C_P(CO_2, g)\ JK^{-1}\ mol^{-1} = 26.0 + 43.5 \times 10^{-3}T - 148.3 \times 10^{-7}T^2$$

$$C_P(H_2O, g)\ JK^{-1}\ mol^{-1} = 30.36 + 9.61 \times 10^{-3}T + 11.8 \times 10^{-7}T^2$$

$$C_P(N_2, g)\ JK^{-1}\ mol^{-1} = 27.30 - 5.23 \times 10^{-3}T - 0.04 \times 10^{-7}T^2$$

Solution

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta H_{298K} = -881.25\ kJ\ mol^{-1} \quad (1)$$

$$H_2O(l) \rightarrow H_2O(g); \quad \Delta H_{298K} = 43.60\ kJ\ mol^{-1} \quad (2)$$

$$2H_2O(l) \rightarrow 2H_2O(g); \quad \Delta H_{298K} = 2 \times 43.60\ kJ\ mol^{-1} = 87.2\ kJ\ mol^{-1} \quad (3)$$

Adding (1) and (3), we get

$$CH_4 + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g); \quad \Delta H_{298K} = -794.05\ kJ \quad (4)$$

Now this energy, i.e. 794.05 kJ liberated by the reaction (4) is not allowed to leave the system and would be used up in heating up one mole of CO_2 (g), 2 moles H_2O (g) and the residual 8 moles of nitrogen of the air. Methane gas is burnt in the calculated amount of air in which O_2 and N_2 are present in the ratio of 1 : 4. Therefore, if T_2 is maximum flame temperature,

$$\Delta H_{heating} = -\Delta H_{reaction} = \int_{298}^{T_2} \sum (nC_P)_f\, dT \quad (3.56)$$

Now,

$$\sum (nC_P)_f = C_P(CO_2) + 2C_P(H_2O) + 8C_P(N_2)$$

$$= 305.12 + 104.56 \times 10^{-3}T - 125 \times 10^{-7}T^2 \quad (3.57)$$

Using Equations (3.57) and (3.56), we have

$$794050 = \left[305.12\,T + \frac{1}{2} \times 104.56 \times 10^{-3}T^2 - \frac{1}{3} \times 125 \times 10^{-7}T^3 \right]_{298}^{T_2}$$

Therefore, $T_2 = 2250$ K. ■

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After having dealt with the first law and its representative applications, we are in a position to discuss the second law of thermodynamics and its applications (refer to Chapter 5). But before we do that, we will discuss the question defining the thermodynamic state of a system (refer to Chapter 4) which will also give rationale behind the equation of state, as in Equations (3.16) and (3.17).

QUESTIONS

1. The oven is at 300°C of heat. What is wrong with this statement.
2. The heat within a gas is evidenced by the random motion of its molecules. What is wrong with this statement?
3. Why is it that only non-ideal gases can be liquefied using Joule–Thomson expansion? Give reasons.
4. The difference between C_P and C_V can be taken to be a measure of compressibility of a substance. Is this statement true or false? In either case give reasons.
5. Internal energy of an ideal gas is a function of temperature only. Show that enthalpy will also be a function of temperature only in case of ideal gas.
6. Perfect vacuum can never be created. An isolated system is also impossible to be created. How are these two statements connected?
7. How the concepts that both enthalpy and internal energy are functions of state are related to the Hess' law of constant heat summation?
8. A system, consisting of an ideal gas, receives heat and also expands under isothermal conditions. How will in this case the energy transferred as heat be related to the work done by the gas during expansion.
9. Water in a bucket is being stirred vigorously. The temperature of water rises inspite of the fact that no heat is being transferred to it. Why?
10. A certain force F when applied to a particle in a system pushes it forward by a distance dx. If you want to measure the magnitude of the work done by (including yourself inside) the system what magnitude you will report? Supplement your answer with reasons.

EXERCISES

3.1 In an experiment, a person does 756 kJ of work on an exercise and looses 94 kJ of energy as heat. What is the internal energy change of the person?

3.2 When an electrical battery is charged by supplying 5×10^5 J of electrical energy, it looses 5×10^4 J of energy as heat to the surroundings. What is the change in internal energy of the battery?

3.3 One mole of an ideal gas confined to a cylinder of volume 2.5 litre at 298 K expands isothermally and reversibly to 5.0 litre. Calculate the work done by the gas.

3.4 The standard heat of combustion of liquid ethanol into carbon dioxide gas and liquid water is -1368 kJ mol^{-1} at constant pressure and at 25°C. Calculate ΔU.

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3.5 Prove that

$$C_P - C_V = \left[V + \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H\right]\left(\frac{\partial P}{\partial T}\right)_V$$

and from this relationship derive $C_P - C_V = nR$ for an ideal gas. [Hint: use $H = U + PV$, $H = H(P, T)$ for an ideal gas $H = H(T)$].

3.6 Prove that

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-(\partial H/\partial P)_T}{(\partial H/\partial T)_P}$$

in case of isoenthalpic process.

3.7 The standard heat of formations of CO_2 (g), H_2O (l) and C_6H_6 (l) are –393.51, –285.83 and 49.0 kJ mol^{-1}, respectively. Find out the standard enthalpy of combustion of C_6H_6 (l).

3.8 If the standard enthalpies of combustion of liquid benzene and liquid cyclohexane are –3268 and –3902 kJ mol^{-1}, respectively. Calculate the standard heat of hydrogenation of liquid benzene to liquid cyclohexane.

3.9 The standard heat of formation of H_2O (l) at 25°C is –285.83 kJ mol^{-1}. What is the standard heat of formation of H_2O (l) at 125°C if the values of molar heat capacities at constant pressure of H_2 (g), O_2 (g) and H_2O (l) are 28.824 JK^{-1} mol^{-1}, 29.355 JK^{-1} mol^{-1} and 76.291 kJ^{-1} mol^{-1}, respectively. Consider that C_P is invariant with temperature.

3.10 The standard heat of formation of NH_3 (g) at 25°C is –46.11 kJ mol^{-1}. What is the heat of formation of NH_3 (g) at 1200°C? Given

$$C_P(N_2, g) = 27.30 + 5.23 \times 10^{-3}T - 0.04 \times 10^{-7}T^2$$

$$C_P(H_2, g) = 29.07 - 0.836 \times 10^{-3}T + 20.1 \times 10^{-7}T^2$$

$$C_P(NH_3, g) = 35.21 + 8.63 \times 10^{-3}T - 8.9 \times 10^{-7}T^2$$

3.11 Calculate the C=C bond, energy in ethylene using the given data

$$2C\ (s) + 2H_2\ (g) \rightarrow C_2H_4\ (g); \qquad \Delta H_1 = 52.26\ kJ$$

$$C\ (s) \rightarrow C\ (g); \qquad \Delta H_2 = 716.68\ kJ$$

$$H_2\ (g) \rightarrow 2H\ (g); \qquad \Delta H_3 = 436\ kJ$$

3.12 Calculate the lattice enthalpy of KBr using the following data and draw the Born–Haber cycle.

(a) Sublimation of K (s); $\Delta H° = +89$ kJ mol^{-1}

(b) Ionization of K (g); $\Delta H° = +418$ kJ mol^{-1}

(c) Vaporization of Br_2 (l); $\Delta H° = 31$ kJ mol^{-1}

(d) Dissociation of Br_2 (g); $\Delta H° = 193$ kJ mol^{-1}

(e) Enthalpy of electron gain of Br (g) to form Br^- (g); $\Delta H° = -325$ kJ mol^{-1}

(f) Enthalpy of formation of solid KBr (s) from its elements, $\Delta H° = -393.8$ kJ mol^{-1}

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Chapter 4

Defining Thermodynamic State: The State Postulate

As stated in Chapter 2, the thermodynamic state of a system is specified by its thermodynamic properties which can be independently varied. Since intensive properties are not dependent on the size (mass) of the system, these can be tabulated or graphed without reference to the amount of the material under study. Therefore, it is of advantage to specify the state of the system by the intensive thermodynamic properties. The state of the system specified in terms of the intensive properties is sometimes called the *intensive thermodynamic state*. To complete the description of the extensive thermodynamic state, addition of a size measure (mass) should be made.

In this context the following important questions are to be answered: (i) What is the number of independent thermodynamic variables (properties) required to specify the state of a system? How does one arrive at this number? And (ii) which properties from amongst the total number of properties should be chosen to specify the state of the system. These questions can be answered if we closely look at the number of ways in which the state of a system can be altered.

Consider a system, consisting of a fixed amount of gas contained in a cylinder fitted with a movable piston, whose state we want to change. Let us see in how many ways we can do it. We can compress the gas and thereby change both volume and energy. We can simultaneously cool the gas to keep its energy fixed and thus change the state at fixed energy, volume being the adjustable variable. One can also keep the volume fixed and adjust the energy independently by heating it or cooling it (i.e. through energy transfer as heat). Thus volume and energy are two independently variable properties. Is it possible to hold volume and energy fixed and alter other thermodynamic properties? No, it is not possible. For example, it is not possible to vary pressure when energy and volume are fixed. If we compress the gas, no doubt the pressure will increase but the volume and energy will also change. If we stir the gas, both pressure and energy will change. Thus the two independently variable properties are volume and energy. If we give up control over energy we can vary pressure and volume independently.

Now let us generalize the observations made above. The change in thermodynamic state is linked with the change in energy of the system. There are only two ways of changing the energy of a system. These are energy transfer as work and energy transfer as heat. The 'work' term has the form $F\,dx$, where F is

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the generalized force and dx is the generalized displacement. If F is independent of the direction of the displacement dx, the amount of energy transferred as work when x is increased by dx will be exactly the same when x is decreased by the same amount dx. This means that the work mode is reversible. We know that the reversible work is most efficient work. The irreversible work mode is inefficient because some energy is always dissipated as heat. That means irreversible work mode is equal to the reversible work mode plus energy transfer as heat. The other notable point about the work term, $F\,dx$, is that it can be integrated unless either a functional relationship between F and x is known or some constraint like F remains constant is imposed. This means that out of the two terms F and x, only one is independent variable. Thus, if there are n reversible work modes operating on the system, the number of independent variables corresponding to the work modes will be equal to n. In addition to the work modes, the energy of the system can also be altered by energy transfer as heat. These considerations lead us to the generalization that the number of independently variable thermodynamic properties, necessary to specify the state of a specified system, is equal to the number of relevant reversible work modes plus one. Here the specified system means a closed system, i.e. having specified amount of specified matter and thermodynamic properties refer to the thermodynamic equilibrium states. This generalization is in fact called the *state postulate*. If the system consists of unit mass of specified system the state postulate should be stated in terms of intensive properties. The statement would then read as "the number of independent intensive thermodynamic properties of a specified system is equal to the number of reversible work modes plus one". It may be mentioned that one can define intensive properties associated with extensive properties. For example, the internal energy per unit mass (specific internal energy, u) and the volume per unit mass (specific volume, v) are written as

$$u = \frac{U}{M} \tag{4.1}$$

and

$$v = \frac{V}{M} \tag{4.2}$$

where M is the mass.

If there are n reversible work modes, according to state postulate, the number of independent thermodynamic properties necessary to specify the state of the system is equal to $(n + 1)$. However, the state postulate does not say that any $(n + 1)$ properties would constitute the independent set. Thus if there is only pressure–volume work operating on the system the number of independent variables required to specify the state of the system is 2 but any two variables do not form the independent set. For example (u, T) will not form the set of independent variables while (u, v) will form the independent set. The specification of u and v fixes the intensive thermodynamic state completely. Temperature, pressure and all other intensive thermodynamic properties for the system would be unique functions of u and v. That is,

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$$T = T(u, v), \quad \text{or} \quad P = P(u, v) \tag{4.3}$$

and similarly

$$u = u(v, T) \quad \text{or} \quad v = v(p, T) \tag{4.4}$$

Thus we have arrived at the rationale behind the equations of the type (3.16) and (3.17) in Chapter 3.

The number of independent thermodynamic variables necessary to specify the state of the system are called *state variables*. Any equation between two or more state variables is called the *equation of state*. For example, the equation $PV = nRT$ and the equations of the type (4.3), (4.4), (3.16) and (3.17) are all equations of state. It hardly needs to be emphasized that knowledge of the state variables of a system is a must for thermodynamic calculations and predictions; the equations of state are supposed to serve this purpose. Every equation in fact is an embodiment of data. Suppose we have an equation $Y = f(X)$ between two variables X and Y. Then we can generate the values of Y from every value of X, of course within the domain of validity of the equation. Since no single equation of state has been discovered till date which will represent data on state variables for all substances in all regions, it has been customary to represent the data on state variables in the form of tables, charts and graphs. These tables, charts and graphs are in fact called *tabular and graphical equations of state* and are very much used by engineers. Any book on engineering thermodynamics has these tabular and graphical equations of state as appendices.

The next natural question is that how these tabular and graphical equations of state are arrived at. The answer is simple, primarily through experiments and by utilizing the several thermodynamic correlations between different variables. The famous Andrew's experiments on carbon dioxide for obtaining pressure–volume relationship at constant temperature are a good example in the present context. The Andrew's experiments in principle are simple (though in actual practice, they were not) wherein carbon dioxide was compressed at several constant temperature and the pressure–volume data were recorded. The Andrew's isotherms for carbon dioxide are reproduced in Figure 4.1.

Let us focus our attention on the isotherm *abcd* corresponding to 13.1°C. The volume decreases as the pressure is increased (see the portion *ab* of the isotherm). As the point *b* is reached the liquefaction starts and at *c* it has been completely liquefied. If the pressure is increased further there is only nominal decrease in volume (the portion *cd* of the isotherm) indicating that liquids are much less compressible in comparison to gases. The isotherm corresponding to 21.5°C, similar to the isotherm at 13.1°C except that the length of the horizontal portion *bc* which represents the region of liquefaction, is less than that in the isotherm corresponding to 13.1°C. As the temperature is raised further, the horizontal portion along which the liquefaction occurs becomes still shorter and at 31.1°C it is merely a point (see point *r* in Figure 4.1). Above 31.1°C, the horizontal portion is totally missing indicating that no liquefaction is possible even with the application of the highest pressure. These experiments convey a very important message, i.e. if one wants to liquefy a gas by pressurization he or she has to first cool it to a certain temperature (which may be characteristic of the gas). This in fact was the discovery of critical temperature. Above the critical temperatures, a

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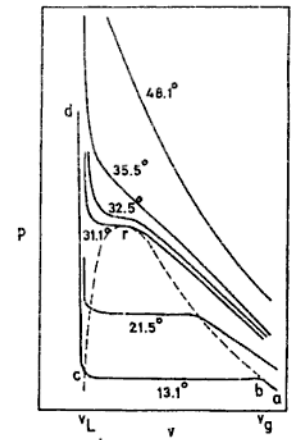

Figure 4.1 Pressure–volume curves of carbon dioxide at different temperatures (°C).

gas cannot be liquefied by pressurization howsoever high may be the magnitude of applied pressure while below the critical temperature (T_C) liquefaction can be brought about by mere pressurization. The pressures and volumes corresponding to critical temperature are called *critical pressure* and *critical volume*, respectively.

The graphs of the type shown in Figure 4.1 are graphical equations of state for carbon dioxide. The graphical equations of state shown in Figure 4.1 can be divided into three distinct regions. These are: (i) the dome-shaped region shown bound by the dotted lines, (ii) the region on the right-hand side of the dome-shaped region, and (iii) the region on the left-hand side of the dome-shaped region. The dotted line *br* is the saturated vapour line (vapour saturated with liquid) and the dotted line *cr* is the saturated liquid line (liquid saturated with vapour). If state of the system is represented by a point on the saturation lines, only one entry point (pressure or volume) is needed to locate this point, i.e. only one degree of freedom. If state of a system is represented by a point either in the right- or in the left-hand side of the dome-shaped region, two entry points (pressure and volume) are needed to locate this point, i.e. two degrees of freedom. However, if state of the system is represented by a point inside the dome where liquid and vapour phases coexist, one also needs to know the composition in addition to pressure and volume to locate this point. The composition can be conveniently represented by the mass fraction of the vapour phase. If M_g and M_L, respectively represent the mass of the substance in the vapour phase and in the liquid phase in the mixed phase region (dome), the mass fraction of the vapour phase x is given by the equation:

$$x = \frac{M_g}{M_L + M_g} \tag{4.5}$$

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The mass fraction of the substance in the liquid phase would be given by $(1 - x)$. The mass fraction x is termed as 'quality' in the texts on engineering thermodynamics. The values of the state variables, for example, specific volume, can be calculated using the equation:

$$v = (1 - x)v_L + xv_g \tag{4.6}$$

The meaning of the terms v_L and v_g are clearly indicated in Figure 4.1. It is not necessary that the graphical equations of state are always on a p–v plane—they can be on T–u plane, T–s (s is entropy) plane, and so on. Then lot of constant property lines, e.g. constant enthalpy line, constant internal energy line, etc., can be drawn on such graphical equations of state. A graphical equation of state is shown in Figure 4.2, as an example.

Before we close this chapter and pass on to the second law in the next chapter let us take up some examples to illustrate the use of Equation (4.6).

EXAMPLE 4.1 Given 2.5 kg of a substance at 7-atm pressure at 165°C in two phase state. If mass fraction of the vapour phase is 0.6, calculate the mass of the substance in the liquid phase and in the vapour phase.

Solution Here

$$M_L = (1 - x)M = (1 - 0.6) \times 2.5 = 1 \text{ kg}$$

and

$$M_g = xM = 0.6 \times 2.5 = 1.5 \text{ kg} \quad \blacksquare$$

EXAMPLE 4.2 If the specific volumes of the saturated vapour (v_g) and saturated liquid (v_L) are respectively 4.43 m^3/kg and 0.0177 m^3/kg at 7-atm pressure and 165°C, what is the total volume occupied by the mixture?

Solution Here

$$\begin{aligned} V = Mv &= [(1 - x)v_L + xv_g]M \\ &= [(1 - 0.6)0.01777 + (0.6)4.43]2.5 \\ &= 6.66 \text{ m}^3 \quad \blacksquare \end{aligned}$$

EXAMPLE 4.3 If the specific internal energies of the saturated vapour (u_g) and the saturated liquid (u_L) are respectively 1105 J/kg and 298 J/kg, what is the total internal energy of the mixture?

Solution We have

$$\begin{aligned} U = Mu &= M[(1 - x)u_L + xu_g] \\ &= 2.5[(1 - 0.6)\ 298 + (0.6)1105] \\ &= 1950 \text{ J} \quad \blacksquare \end{aligned}$$

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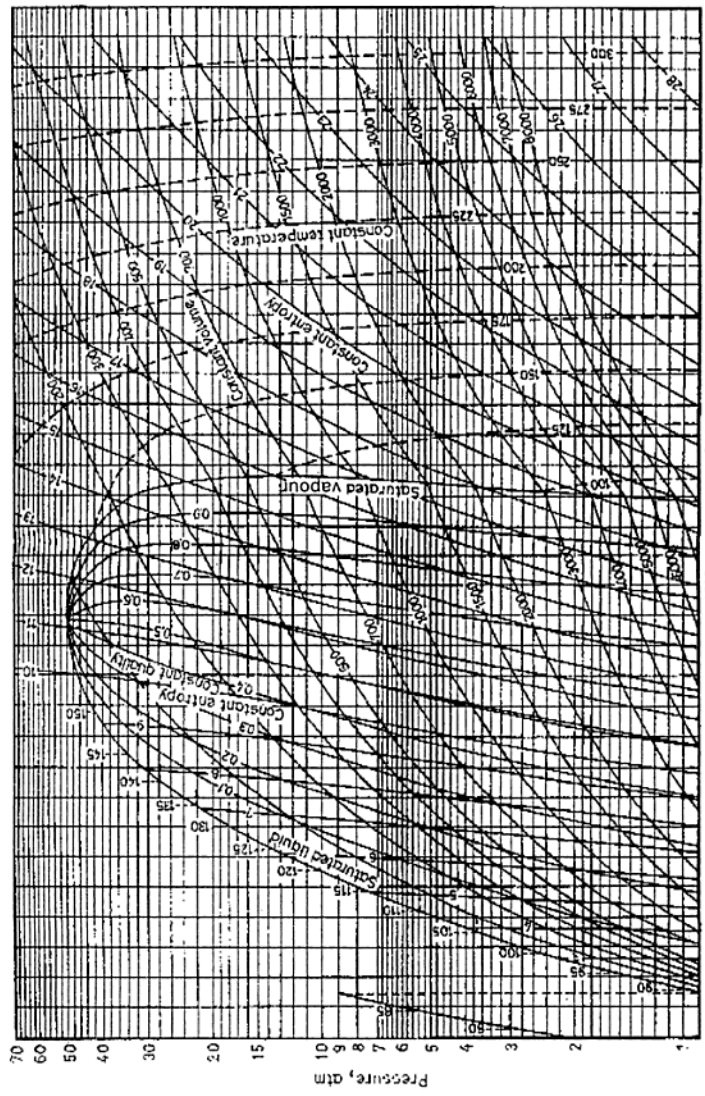

Figure 4.2 Thermodynamic properties of oxygen. From NBS D-2573 1 cal = 4.184 Joules, v in mL/g mole, T in K, S in cal/g mol-K.

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QUESTIONS

1. Can changes of state occur within a system without energy transfer across the boundaries?
2. Suppose the energy of a closed system has been changed by n irreversible work modes. How many state variables will the system have?
3. Why is it not true that

$$\rho = (1 - x)\rho_f + x\rho_g$$

where ρ is the mass density, f and g denote the liquid and the gaseous state.

4. When you inflate a balloon at constant temperature, pressure increases and the volume also increases. How would you explain the apparent violation of the equation of state, $PV = Constant$?
5. Show that the quantity $\partial U/\partial V$, where U is the internal energy and V is the volume, has the dimensions of pressure. What is this pressure called and what this pressure is due to? What would be its value for a perfect gas?

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Chapter 5

The Second Law of Thermodynamics

The first law of thermodynamics is just a particular case of the generalized law of conservation of energy. Historically, it is a consequence of failure of the efforts made by greedy humans to create energy out of nothing. Having failed in this, people tried to achieve the next best, i.e. to achieve a total conversion of disorganized energy (internal energy) into an organized energy (work). Here again they failed. The second law of thermodynamics owes its origin to these failures. But one good thing happened as a consequence of these efforts. These were the time of James Watt. Lots of improvements were being made in the steam engines. At this juncture, a young French engineer Sadi Carnot (1824) made a radical generalization which disillusioned all those who were trying for hundred per cent conversion of the disorganized energy to the organized energy by incorporating mechanical improvements in the steam engines. Carnot proved that even in the highly idealized system the hundred per cent conversion was impossible to achieve.

Before we take up the Carnot's generalization and the emergence of the second law from it let us introduce a term called 'spontaneous process' and its meaning. The concept of spontaneous process as we will see gives us an overall idea of the need for the second law in the structure of thermodynamics.

5.1 SPONTANEOUS PROCESS

Spontaneous processes are those which occur of their own accord. For example, water flows from a higher pressure to a lower pressure, heat flows from a higher temperature to a lower temperature, carbon burns in air to give carbon dioxide and energy, we all grow older with time etc. Remember spontaneous processes are not instantaneous processes. It simply means that a change is favourable in a particular direction. Have you ever thought how easy it is to reverse these processes? Can heat and water flow uphill of their own accord? Can carbon dioxide give us back carbon and oxygen? Can we again become young? These reverse processes may not be impossible but certainly they are not spontaneous. They cannot occur of their own accord. Thus, spontaneous processes are also irreversible processes. The first law is helpless to reveal the possibility or impossibility of a process. It is simply a balance sheet of energy transactions and cannot point out the direction of time. Nevertheless, if thermodynamics is to have predictive value it should have the ability to rule out the impossible processes and predict the direction of a

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change. The second law of thermodynamics provides the necessary structure for this type of analysis.

5.2 CARNOT'S ENGINE

We have seen an steam engine (a locomotive) working. It essentially operates as follows: A source of heat is used to heat steam which is the working substance. The hot steam through a valve enters a piston cylinder system and expands to push the piston forward which in turn drives a flywheel with which it is mechanically coupled. After the steam has lost its expansive power and cooled down the flywheel due to its inertia of motion returns the piston to its original position pushing the cooled steam out through a valve. The fresh hot steam again enters the piston cylinder system to push the piston forward and so on. The efficiency, e of such engines can be defined as

$$e = \frac{\text{Work done by the system}}{\text{Heat absorbed from heat source}} \tag{5.1}$$

The maximum value of e cannot be greater than unity because then it would mean more than hundred per cent conversion of disorganized energy (heat absorbed) into organized energy (work). The question is whether it is possible to achieve the value of e equal to 1.

To prove this point, Carnot considered a highly idealized engine; the idealization made were to the extent that it becomes a hypothetical machine. All the steps envisaged were perfectly reversible, equilibrium at all points of time, all processes carried out extremely slowly (in infinite time), etc. In this hypothetical engine the working substance is one mole of an ideal gas; it is contained in a cylinder fitted with a piston. The piston is weightless and there is absolutely no friction anywhere. There are two infinitely large heat reservoirs at temperatures T_2 and T_1, T_2 being greater than T_1. The temperature T_2 of the source and the temperature T_1 of the sink naturally remain constant in time. It is assumed that completely adiabatic processes can be carried out whenever required by surrounding the cylinder with a perfectly non-conducting jacket. The various stages of the cycle executed by this engine can be represented on P–V plane (indicator diagram). The four stages of the cycle are represented in Figure 5.1.

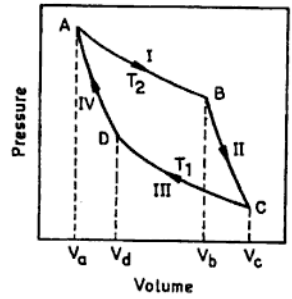

Figure 5.1 The Carnot cycle.

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Stage 1. The cylinder containing one mole of the ideal gas having volume V_a is placed in contact with the heat reservoir at temperature T_2. The external pressure and the temperature of the gas are only infinitesimally less than the gas pressure and the temperature of reservoir respectively to make the isothermal reversible expansion of the gas possible in principle. Thus the gas expands isothermally and reversibly to a final volume V_b beyond which it cannot expand isothermally. The process is represented by the isotherm AB (Figure 5.1). The work done (W_1) by the gas is given by

$$W_1 = \int_{V_a}^{V_b} P\,dV = RT_2 \int_{V_a}^{V_b} \frac{dV}{V} = RT_2 \ln \frac{V_b}{V_a} \tag{5.2}$$

and the heat Q_2 absorbed by the gas can be calculated using first law equation $Q_2 = W_1 + \Delta U$. Since for an ideal gas U is a function only of temperature, for an isothermal process (curve AB of Figure 5.1) $\Delta U = 0$. Therefore,

$$Q_2 = W_1 = RT_2 \ln \frac{V_b}{V_a} \tag{5.3}$$

Stage 2. After the maximum expansion under isothermal conditions is achieved, the contact between the heat reservoir at temperature T_2 and the cylinder is removed and the cylinder is thermally insulated so that adiabatic conditions prevail; no heat enters or leaves the gas inside the cylinder. Now the gas is made to expand adiabatically and reversibly (at an infinitely slow rate) till it attains the maximum volume V_c. From the first law, it follows that the work done W_2 along the adiabatic path BC is given by

$$0 = \Delta U + W_2 \tag{5.4}$$

During the adiabatic expansion, the gas inside the cylinder cools down to temperature T_1. Using the relationship

$$\Delta U = C_V(T_1 - T_2) \tag{5.4a}$$

we can write from Equation (5.4)

$$W_2 = -C_V(T_1 - T_2) = C_V(T_2 - T_1) \tag{5.5}$$

In Equation (5.4a), T_1 and T_2 are so close to each other that the value of C_V does not vary with temperature. The heat absorbed during the adiabatic expansion is zero.

In order that the gas inside the cylinder which has lost all its expansive power may be reused[3], it should be brought back to its initial state. This is achieved through stages 3 and 4.

Stage 3. The thermal insulation around the cylinder is then removed and the gas inside the cylinder is brought in contact with the heat sink at temperature T_1 —the environment at temperature T_1 may be visualized heat sink. The gas is now compressed isothermally and reversibly from the initial volume V_c to a final

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volume V_d. Since the working substance is an ideal gas whose internal energy is the function of temperature only, we can write, using first law for the work done on the gas (W_3) and the heat evolved Q_1 at temperature T_1

$$-Q_1 + W_3 = 0$$

But

$$W_3 = \int_{V_c}^{V_d} -P\,dV = -RT_1 \int_{V_c}^{V_d} \frac{dV}{V} = RT_1 \ln \frac{V_c}{V_d} \tag{5.6}$$

Therefore,

$$Q_1 = RT_1 \ln \frac{V_c}{V_d} \tag{5.7}$$

Stage 4. The cylinder is finally removed from the heat sink at temperature T_1 and is thermally insulated so that adiabatic conditions prevail. The gas is then adiabatically and reversibly compressed till it attains its initial volume V_a and initial temperature T_2. It is obvious that the heat absorbed along the adiabatic path DA is zero. The work done W_4, on the gas, along the path DA, can be worked out using the first law. Thus we can write,

$$0 + W_4 = \Delta U = C_V(T_2 - T_1) \tag{5.8}$$

Now the work done W by the gas in the entire cycle $ABCDA$ (Figure 5.1) can be written as

$$W = W_1 + W_2 - W_3 - W_4 \left(+W_3 \text{ and } +W_4 \text{ are work done on the gas}\right)$$

or

$$W = RT_2 \ln \frac{V_b}{V_a} + C_V(T_2 - T_1) - RT_1 \ln \frac{V_c}{V_d} - C_V(T_2 - T_1) \tag{5.9}$$

$$= RT_2 \ln \frac{V_b}{V_a} + RT_1 \ln \frac{V_d}{V_c} \tag{5.10}$$

Since V_a and V_d lie on same adiabatic curve AD and V_b and V_c lie on same adiabatic curve BC, it can be easily shown[1] that

---

1. For reversible adiabatic compression, we have from the first law

$$0 + W = \Delta U \quad \text{or} \quad -P\,dV = C_V\,dT$$

For ideal gas

$$C_V\,dT = -RT\frac{dV}{V} \quad \text{or} \quad C_V\,d\ln T = -R\,d\ln V$$

Integrating between the initial and final limits 1 and 2 and using $C_P - C_V = R$ for an ideal gas, we have

$$C_V \log \frac{T_2}{T_1} = R \log \frac{V_1}{V_2} = (C_P - C_V) \log \frac{V_1}{V_2} \quad \text{or} \quad \log \frac{T_2}{T_1} = \left(\frac{C_P}{C_V} - 1\right) \log \frac{V_1}{V_2} = (\gamma - 1) \log \frac{V_1}{V_2}$$

From the above equation, it follows that

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

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$$\left(\frac{T_2}{T_1}\right)=\left(\frac{V_d}{V_a}\right)^{\gamma-1} \quad \text{and} \quad \left(\frac{T_2}{T_1}\right)=\left(\frac{V_c}{V_b}\right)^{\gamma-1}$$

where $$\gamma=\frac{C_P}{C_V}$$

In other words,

$$\frac{V_d}{V_a}=\frac{V_c}{V_b} \quad \text{or} \quad \frac{V_b}{V_a}=\frac{V_c}{V_d} \tag{5.11}$$

From Equations (5.10) and (5.11), it follows that

$$W=R\left(T_2-T_1\right)\ln\frac{V_b}{V_a} \tag{5.12}$$

Efficiency (e) of the reversible Carnot engine is given by $e = W/Q_2$. Substituting the values of W and Q_2 from Equations (5.12) and (5.3) respectively, we can write

$$e=\frac{T_2-T_1}{T_2}=1-\frac{T_1}{T_2} \tag{5.13}$$

Equation (5.13) is one of the most radical generalizations in thermodynamics. The essence of the second law of thermodynamics and also of the third law of thermodynamics resides in this result. A close scrutiny of Equation (5.13) would reveal the following:

(a) Even in an highly-idealized engine like Carnot's engine, the efficiency, e of energy conversion cannot be equal to unity, i.e. complete conversion of disorganized energy to organized energy is not possible. Wastage can be minimized but not eliminated completely. These statements contain the essence of the second law. A little consideration would show that the well-known statements like "friction between two bodies can never be zero" or "perfect vacuum can never be created" etc., would follow as a corollary.

(b) One can question the statements in (a) above. Equation (5.13) reveals that $e = 1$ when $T_1 = 0$. That means $T_1 = 0$ is the lowest temperature conceivable (absolute 0) because $e > 1$ is unthinkable. Thus, Equation (5.13) gives us a reference point on which to define a temperature scale. This has actually been done by Lord Kelvin. Such a temperature scale is called the *thermodynamic scale.*

The fact that e can be equal to unity, at least in principle, at $T_1 = 0$, could have been one motivation for the attempts made towards production of low temperatures. Consequent to such efforts came an inductive generalization known as the third law of thermodynamics which reads as "It is impossible by any procedure no matter how idealized to reduce the temperature of any system to the

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absolute zero in finite number of operations".[2] Thus, unattainability of absolute zero of temperature is closely linked with Equation (5.13) and also with the generalization that wastage in any energy conversion machine can never be reduced to zero. We will take up discussion of the third law a little later.

(c) The efficiency of energy conversion (e) in a Carnot engine is independent of the nature of the working substance and is a function only of the two temperatures—temperature of the heat source and temperature of the heat sink—between which it works. i.e.

$$e = f(T_1, T_2) \tag{5.14}$$

It can, therefore, be concluded that reversible Carnot cycles operating between the same initial and final temperatures must have the same efficiency. This is well known Carnot's theorem and will be discussed in a short while from now.

(d) No engine can have an efficiency greater than the corresponding Carnot engine.

EXAMPLE 5.1 A carnot engine working between 100°C and 300°C absorbs 750 J heat from the high-temperature source. Calculate the work done by the engine, heat rejected and efficiency of the engine.

Solution We have

$$\text{Efficiency } e = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} = \frac{573 - 373}{573} = \frac{200}{573} = 0.349$$

Therefore,

$$\text{Efficiency of the engine} = 0.349$$

and

$$\text{Work done by the engine} = 0.349 Q_2 = 0.349 \times 750 \text{ J} = 262 \text{ J}$$

Let heat rejected by the engine be Q_1. Therefore,

$$\frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad \text{or} \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad Q_1 = \frac{T_1 Q_2}{T_2}$$

Thus

$$\text{Heat rejected by the engine} = \frac{373}{573} \times 750 \text{ J} = 488 \text{ J} \quad \blacksquare$$

5.3 CARNOT'S THEOREM

To prove this theorem we shall proceed in the following way. Suppose we have two reversible engines, say I and II, which are working between the same initial and final temperatures but have different efficiencies. Let us suppose for the sake

2. Quoted from Fowler and Guggenheim, *Statistical thermodynamics*, Cambridge University Press, 1940, p. 224.

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of argument that engine I is more efficient than engine II. Since both engines are perfectly reversible let us conceptually think that the two engines are coupled in such a way that they are working in the directions opposite to each other. That is to say, the engine I extracts heat Q_2 from the source at temperature T_2, does some work $(-W)$ on the environment and returns the remaining heat Q_1 to the heat sink at temperature T_1, whereas the engine II which is working in the reverse direction extracts some heat Q_1' from the heat sink at temperature T_1 and work W' is done on the engine and finally it returns the heat Q_2 to the heat source at temperature T_2. Since the engine II is supposed to be less efficient than engine I, while working in the same direction as engine I, it would extract the same amount of heat Q_2 from the source and would do less work on the environment $(-W')$ than is done by the engine I and would therefore return more heat to the sink at temperature T_1 than is returned by the engine I. The situation of the composite engine (I + II) in which the two engines are working in the direction opposite to each other, the engine I working in the direct manner and the engine II working in the reverse manner, is depicted in Figure 5.2.

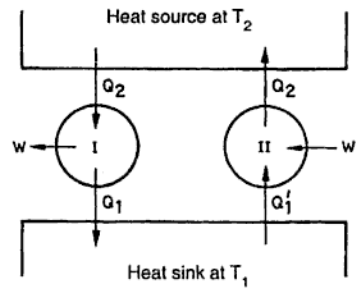

Figure 5.2 Proof of Carnot theorem.

The balance sheet of energy transaction for the two engines in the composite engine (I + II) can be written as follows:

Engine I	Engine II
Energy transfer as heat at temperature T_2 to the engine = Q_2	Energy transfer as heat at temperature T_2 from the engine = $-Q_2$
Work done by the engine on the environment = $-W$	Work done on the engine by the environment = W'
Energy transfer as heat at temperature T_1 from the engine = $-Q_1$	Energy transfer as heat at temperature T_1 to the engine = Q_1'

Thus the net situation for the composite engine I + II can be written as follows: Energy transfer as heat at temperature T_2 to the engine = $Q_2 - Q_2 = 0$. Work done by the engine = $(W - W')$ (the negative sign as per sign convention is for the work done by the system). Energy transfer as heat at temperature T_1 to the engine = $Q_1' - Q_1$.

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Thus the composite engine (I + II) does not extract any heat from the heat source at T_2. On the contrary, it extracts all the heat from the heat sink (environment) at temperature T_1 and performs the work $(W - W')$ on the environment. It also achieves the complete conversion of disorganized energy into work, i.e. no wastage at all. Though there is nothing contrary to the first law in this result because the machine has nowhere acted as energy creator, this result, nevertheless, is too good to be true. Let us think what it would imply. It would not be necessary for a ship or an aeroplane, or an automobile or a locomotive to carry fuel. It can extract all the needed energy from the environment, which is an infinitely large revervoir of energy, and can go on running indefinitely. The entire human experience forbids us to agree to such a proposition. Not only is the Carnot's theorem that "it is impossible for two reversible Carnot cycles operating between the same initial and final temperatures to have different efficiencies" is proved, it is also proved that heat cannot travel from a colder body to a hotter body of its own accord, the complete (I + II) as shown in Figure 5.2 acts by extracting heat from the heat sink (environment). Thus the following statements can be made.

(a) It is impossible by a cyclic process to take heat from a reservoir and convert it into work without, in the same operation, transferring heat from a hot to a cold reservoir.

(b) It is impossible by a cyclic process to transfer heat from a colder to a warmer reservoir without net changes in other bodies. In other words, heat cannot spontaneously pass from a colder to a warmer body.

These statements are the statements of the second law of thermodynamics. The first statement is due to Thomson and the second one is due to Clausius. The second law can be stated in several other forms. All these statements are corollaries of each other.

EXAMPLE 5.2 An inventor claims to have perfected an engine which will produce power from energy transferred as heat from a 1000 K flame. Energy will be rejected as heat to the ground at 250 K. He claims a 80% energy conversion efficiency. As chief patent officer would you issue him a patent? Give your reasons.

Solution The efficiency of engine cannot exceed the efficiency of the corresponding Carnot's engine. In this case the Carnot's efficiency e is given by

$$e = 1 - \frac{T_1}{T_2}$$

where T_1 and T_2 are the temperatures of the heat sink and the heat source respectively. Hence

$$e = 1 - \frac{250}{1000} = 1 - 0.25 = 0.75 \text{ or } 75\%$$

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Therefore, the inventors claim of 80% efficiency is absurd. The patent application should be rejected. ■

EXAMPLE 5.3 A heat engine is working between 150°C and 50°C. What is the minimum heat withdrawal from heat source to yield 1.3 kJ of work?

Solution We have

$$\text{Efficiency } e = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} = \frac{423 - 323}{423} = \frac{100}{423} = 0.236$$

Therefore,

$$\text{minimum heat withdrawal from heat source } Q_2 = \frac{W}{0.236} = \frac{1.3 \text{ kJ}}{0.236} = 5.51 \text{ kJ} \quad ■$$

5.4 ENTROPY

Let us consider an ideal gas undergoing a reversible compression from an initial state (T_1, V_1) to a final state (T_2, V_2). The first law statement for an infinitesimal change can be written as

$$dQ_{\text{reversible}} + dW_{\text{reversible}} = dU$$

or

$$dQ_{\text{reversible}} - P\,dV = dU \tag{5.15}$$

or

$$dQ_{\text{reversible}} = dU + P\,dV$$

Since $dU = C_V\,dT$, Equation (5.15) can be rewritten as

$$dQ_{\text{reversible}} = C_V\,dT + P\,dV = C_V\,dT + \frac{nRT}{V}dV \tag{5.16}$$

In Equation (5.16), though the first term on the right-hand side is in general integrable within limits, the second term, $P\,dV$, is not because of its path-dependent nature. Thus $dQ_{\text{reversible}}$ is not an exact differential because the condition (2.4) or (2.5) is not satisfied, i.e.

$$\frac{\partial C_V}{\partial V} \neq \left[\frac{\partial (nRT/V)}{\partial T}\right]_V$$

However, if Equation (5.16) is multiplied throughout by $1/T$, i.e.

$$\frac{dQ_{\text{reversible}}}{T} = C_V \frac{dT}{T} - nR\frac{dV}{V} \tag{5.17}$$

both terms on the right-hand side become integrable in general. Thus,

$$\int_1^2 \frac{dQ_{\text{reversible}}}{T} = \int_1^2 C_V \frac{dT}{T} + nR\int_1^2 \frac{dV}{V} = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \tag{5.18}$$

The important point that emerges is that though $dQ_{\text{reversible}}$ is in general not integrable $dQ_{\text{reversible}}/T$ is. Since $dQ_{\text{reversible}}/T$ can be integrated within limits, it should

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be a function of state, a path-independent quantity, i.e. an exact differential. This was first recognized by Clausius who gave the name entropy to this function of state and symbolised it by the letter S. Thus Equation (5.18) would be read as

$$\int_1^2 dS = \int_1^2 \frac{dQ_{\text{reversible}}}{T} = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \tag{5.19}$$

The statement that $\int_1^2 dQ_{\text{reversible}}$ is dependent on path, whereas $\int_1^2 dQ_{\text{reversible}}/T$ is independent of path in itself an alternative statement of the second law of thermodynamics. The arguments presented above, though based on ideal gas, are quite general and hence can be extended to any other system.

Since S is a state function, it follows that

$$\text{(reversible)} \quad \oint dS = \int_1^2 dS + \int_2^1 dS = S_2 - S_1 + S_1 - S_2 = 0$$

It is also obvious from Equation (5.19) that area under the curve on a T–S plane is a measure of the heat added to or withdrawn from the system reversibly. In fact the T–S diagrams for representing thermodynamic changes are often used in engineering problems. The indicator diagram on P–V plane, for the Carnot's cycle, when drawn on the T–S plane would look like one shown in the Figure 5.3.

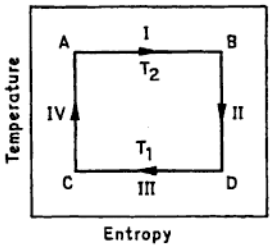

Figure 5.3 Carnot cycle on a T–S plane.

It is obvious that there would be no change of entropy along the adiabatics and no change of temperature along the isotherms.

EXAMPLE 5.4 Using Carnot cycle show that the integral of $dQ_{\text{reversible}}/T$ around a cycle is zero.

Solution The integral in this case is the sum of the heat transferred in two isothermal processes. In case of adiabatic processes heat transfer is equal to zero. From Section 5.2, we have

$$\oint \frac{dQ_{\text{reversible}}}{T} = \frac{dQ_2}{T_2} + 0 - \frac{dQ_1}{T_1} + 0$$

$$= R \ln \frac{V_b}{V_a} - R \ln \frac{V_c}{V_d}$$

$$= R \ln \frac{V_b/V_a}{V_c/V_d}$$

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But

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

Therefore,

$$\oint \frac{dQ_{\text{reversible}}}{T} = R \ln 1 = 0 \qquad \blacksquare$$

EXAMPLE 5.5 What is the molar entropy change when argon gas at 25°C in a container of 500 cm^3 expands isothermally to 1000 cm^3?

Solution We have

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Here process is isothermal, hence $T_1 = T_2$. Therefore,

$$\Delta S_T = nR \ln \frac{V_2}{V_1} = 1 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \ln \frac{1000}{500} = 5.8 \text{ JK}^{-1} \qquad \blacksquare$$

EXAMPLE 5.6 What is the change in molar entropy when a gas expands isothermally and reversibly at 298 K; the work done by the system is 1.728 kJ mol^{-1}.

Solution For isothermal process, we have

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

We also know from reversible work

$$w = nRT \ln \frac{V_2}{V_1}$$

Therefore, $w = T\Delta S$. Thus,

$$\Delta S = \frac{w}{T} = \frac{1.728 \text{ kJ mol}^{-1}}{298 \text{ K}} = 5.8 \text{ JK}^{-1} \text{ mol}^{-1} \qquad \blacksquare$$

5.5 THE CLAUSIUS INEQUALITY

The equation

$$\oint dS = \oint \frac{dQ_{\text{reversible}}}{T} = 0 \tag{5.20}$$

is valid for a reversible cycle. Clausius showed that if any part of the cycle is irreversible,

$$\text{(irreversible)} \oint \frac{dQ}{T} < 0 \tag{5.21}$$

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The proof of the inequality (5.21) follows from the fact that the efficiency of an irreversible Carnot's cycle is always less than that of a reversible cycle working between the same initial and final temperatures. In the reversible cycle, the isothermal expansion yields the maximum work and the isothermal compression requires the minimum work so that the efficiency is maximum in the reversible case. Therefore, for the irreversible case (refer to Equations (5.2 to 5.13)),

$$e = \frac{W}{Q_2} = \frac{W_1 - W_3}{Q_2} = \frac{Q_2 + Q_1}{Q_2} < \frac{T_2 - T_1}{T_2} \tag{5.22}$$

Hence

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} < 0 \tag{5.23}$$

Thus instead of Equation (5.20) which applies to the reversible case, we get the inequality (5.21).

5.6 ENTROPY CHANGES IN ISOLATED SYSTEMS

The change in entropy in going from state 1 to state 2 is always the same whatever be the path between 1 and 2. This is because entropy a function of the state of the system alone. It hardly matters whether the path is reversible or irreversible. When the path is reversible,

$$dS = \frac{dQ_{\text{reversible}}}{T}$$

That is,

$$S_2 - S_1 = \int_1^2 \frac{dQ_{\text{reversible}}}{T} \tag{5.24}$$

In a completely isolated system, the adiabatic conditions prevail of necessity, because no heat can enter or leave the system. If the process going on in the isolated system is reversible,

$$dS = \frac{dQ_{\text{reversible}}}{T} = 0 \quad \text{because} \quad dQ_{\text{reversible}} = 0$$

It follows therefore for a reversible process in isolated system, S = constant. This implies that if in one part of the system entropy increases it must decrease in some other part of the system so that the net effect is, S = constant. An illustration of this result can be found in the following discussion.

The transfer of heat from a hot body (temperature T_2) to a colder body (temperature T_1) is essentially an irreversible process but it can be made to occur reversibly using an ideal gas. The gas is first placed in contact with the hot body (temperature T_2) and allowed to expand isothermally and reversibly. In this process the gas extracts a heat Q from the hot body. The implied assumption is that the heat capacities of the bodies are so large that on adding heat to them or withdrawing heat from them does not affect their temperature to any measurable

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extent. The gas is then removed from the contact with the hot body and is made to expand adiabatically and reversibly till its temperature falls to T_1. The gas is then placed in contact with the colder body and is compressed isothermally and reversibly till it gives the heat Q which it originally extracted from the hot body, to the colder body. The balance sheet of this transaction can be written as follows:

$$\text{Loss of entropy by the hot body} = \frac{Q}{T_2}$$

and

$$\text{Gain of entropy by the cold body} = \frac{Q}{T_1}$$

Then

$$\text{Hence net gain } \Delta S = \frac{Q}{T_1} - \frac{Q}{T_2} \tag{5.25}$$

Since $T_2 > T_1$, $\Delta S > 0$. The entropy of the ideal gas has decreased by the same amount. Therefore, for the entire isolated system consisting of hot body plus gas plus cold body $\Delta S = 0$ for the reversible process. If we had carried out the transfer of heat irreversibly simply by placing the hot body in direct contact with the cold body there would have been no compensating entropy decrease as observed in the case when ideal gas was used. The entropy of the isolated system would (consisting of hot body and cold body) have increased by the amount

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

The one very important point which must be recognized here is that the system plus environment is always considered an isolated system. For example, the ideal gas used in the reversible transfer of heat from the hot to the colder body considered above is part of the environment while the hot body and the colder body are part of the system and the hot body plus cold body plus the ideal gas constitutes the entire isolated system.

If this point is not recognized, a serious confusion would arise. Entropy is a function of state and therefore the value of ΔS should be same whether the path between the initial and final state is reversible or irreversible. It appears as if this is contradicted by the result obtained above, i.e. for reversible process in isolated system $\Delta S = 0$ and for irreversible processes in isolated system $\Delta S > 0$. This apparent contradiction would disappear if we consider system plus environment as the isolated system. The entropy change for the isolated system includes the changes in the system as well as in the environment and total entropy change is called the *entropy change for the universe*. Thus

$$\Delta S \text{ (universe)} = \Delta S \text{ (system)} + \Delta S \text{ (environment)} \tag{5.26}$$

The value of ΔS (system) is the same whether the process is reversible or irreversible. It is the ΔS (environment) which is different for reversible and irreversible changes. We also have for an isolated system, $dS \geq 0$.

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The equality holding for the reversible process and the inequality holding for the irreversible process can be arrived at in another simple way. Let us consider a closed system which does reversible work $dW_{\text{reversible}}$ and irreversible work $dW_{\text{irreversible}}$ on the environment. It is well-known that

$$dW_{\text{reversible}} > dW_{\text{irreversible}} \tag{5.27}$$

Since internal energy U is a function of state, the value of dU should not depend upon the reversibility or irreversibility of the operation. That is

$$dU = dU_{\text{reversible}} = dU_{\text{irreversible}} \tag{5.28}$$

Now using first law, we can write

$$dU = dQ_{\text{reversible}} - dW_{\text{reversible}} \tag{5.29}$$

and

$$dU = dQ_{\text{irreversible}} - dW_{\text{irreversible}} \tag{5.29a}$$

where $dQ_{\text{reversible}}$ and $dQ_{\text{irreversible}}$ represent the heats received by the system from the environment under reversible and irreversible conditions, respectively.

From Equations (5.29) and (5.29a) and the inequality (5.27), it follows that

$$dQ_{\text{reversible}} - dQ_{\text{irreversible}} = \left(dQ_{\text{reversible}} - dW_{\text{irreversible}}\right) > 0 \tag{5.30}$$

Thus

$$dQ_{\text{reversible}} > dQ_{\text{irreversible}} \quad \text{or} \quad \frac{dQ_{\text{reversible}}}{T} > \frac{dQ_{\text{irreversible}}}{T}$$

Since $dS = dQ_{\text{reversible}}/T$, we have

$$dS > \frac{dQ_{\text{irreversible}}}{T} \tag{5.31}$$

or

$$dS > \frac{dU + dW_{\text{irreversible}}}{T} \tag{5.32}$$

and

$$dS = \frac{dU + dW_{\text{reversible}}}{T} \tag{5.33}$$

Since there is no exchange of energy, matter, heat etc., across the boundaries of an isolated system, i.e. $dQ = 0$, $dU = 0$, $dW = 0$, it follows from Equations (5.32) and (5.33) that for an isolated system

$$dS = 0 \quad \text{(for reversible process)} \tag{5.34}$$

$$dS > 0 \quad \text{(for irreversible process)} \tag{5.35}$$

Since all naturally occurring processes are irreversible, any change that occurs spontaneously in nature is accompanied by a net increase in entropy. This led Clausius to state that "The energy of the universe is constant; the entropy of the universe tends always towards a maximum". If there is any conceivable process for which $dS > 0$ a system will be subject to spontaneous change. If we consider

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universe as an isolated system the condition of entropy maximization contained in the Clausius's statement is in fact a condition for equilibrium applicable to all conceivable changes taking place in all the system in the world considered together. The entropy goes on increasing with time and ultimately becomes constant (maximizes). The condition for the system where only mechanical work is allowed can be written as

$$(dS)_{U,V} = 0 \tag{5.36}$$

The constant U and V conditions indicate that the system is isolated. Equation (5.36) represents the condition of entropy maximization. As a corollary of Equation (5.36) it follows that

$$(dU)_{S,V} = 0 \tag{5.37}$$

Equation (5.37) which represents the condition of internal energy minimization also represents a condition for equilibrium. The system maintained at constant entropy and volume will attain equilibrium at a state of minimum internal energy.

The statement of Clausius on the continuously increasing character of entropy has interesting philosophical implications. Eddington suggested that because of its continuously increasing character the entropy could be the physical basis of our concept of time; Eddington suggested that "entropy is time's arrow". Since entropy of the universe is constantly increasing the origin of universe should correspond to $S = 0$.

EXAMPLE 5.7 The standard reaction enthalpy is ($\Delta H°$) for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at 25°C is –92.22 kJ. What is the change in entropy of the surroundings at 25°C when the reaction takes place at constant pressure?

Solution Standard reaction enthalpy is –92.22 kJ. Therefore, heat gained by surroundings at 25°C is 92.22 kJ. Hence

$$\text{Change in entropy of the surroundings at 25°C} = \frac{92.22 \times 10^3 \text{ J}}{298 \text{ K}} = 309.5 \text{ JK}^{-1} \blacksquare$$

5.7 ENTROPY AND RANDOMNESS

Entropy is said to be a measure of the randomness in a system consisting of atoms and molecules. More is the randomness, larger is the value of entropy. 'Entropy' is also said to be a measure of unavailable energy—unavailable for doing macroscopic work. These statements about the entropy are consistent with the observations. (i) In a cyclic process total conversion of heat into work is not possible. (ii) The efficiency of a working engine is never equal to 1 etc. The main question that crops up is that when a gas contained in a cylinder fitted with a movable piston is heated, why is all the heat absorbed by the gas is not converted into mechanical work even if there is no friction between piston and cylinder? Where does the unused energy go? These questions can be answered with the help of the following simple example [refer to Figures 5.4(a) and 5.4(b)].

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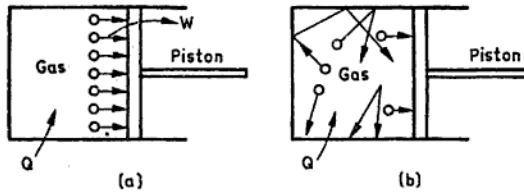

Figure 5.4 Conversion of heat to work: (a) total conversion, (b) partial conversion. It is assumed that there is no friction between piston and cylinder.

The heat absorbed by the gas increases the kinetic energy of the molecules of the gas. Only those molecules of the gas which strike the piston perpendicularly succeed in pushing the piston forward and thus doing work. If all the heat absorbed by the gas were to be converted into mechanical work it would be necessary for all the molecules to strike the piston perpendicularly (Figure 5.4a). This, however, does not happen. The heat absorbed by the gas though enhances the kinetic energy of the molecules, the molecules move at random, of course, with higher velocities (Figure 5.4b). If the situation of the kind shown in Figure 5.4(a) is to prevail, the molecules in the gas would be required to be present in one particular configuration. The main question, therefore, is what is the probability of getting this particular configuration. The probability of getting this particular configuration would be closely related to the probability of getting hundred per cent conversion of heat to work.

EXAMPLE 5.8 Calculate the entropy change when one mole of argon gas is heated from 25°C to 300°C at constant volume. Given C_V of argon gas = 29.1 JK^{-1} mol^{-1}.

Solution We know

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Here volume is constant, therefore, $V_1 = V_2$. Hence

$$\Delta S_V = nC_V \ln \frac{T_2}{T_1} = 1 \text{ mol} \times 29.1 \text{ JK}^{-1} \text{ mol}^{-1} \ln \frac{573}{298} = 19.03 \text{ JK}^{-1} \quad \blacksquare$$

EXAMPLE 5.9 Calculate the total entropy change when 200 g of solid benzene is heated from 3°C to 100°C. Assume that C_P does not change within this temperature limit. Given data for benzene are: freezing point = 5.7°C, boiling point = 80.3°C, standard enthalpy of fusion, $\Delta_{\text{fusion}}H°$ = 9.87 kJ mol^{-1} standard enthalpy of vaporization $\Delta_{\text{vapour}}H°$ = 30.8 kJ mol^{-1}, C_P = 136.1 JK^{-1} mol^{-1} molecular weight of benzene = 78 g/mol.

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Solution We know

$$dQ_{\text{reversible}} = dU + P\,dV = dH - P\,dV - VdP + P\,dVd = dH - VdP$$

Since $U = H - PV$. Therefore,

$$dQ_{\text{reversible}} = nC_P dT - \frac{nRT}{P} dP$$

Dividing both sides by T and then integrating under given limits, we get

$$\int_1^2 \frac{dQ_{\text{reversible}}}{T} = \Delta S = \int_{T_1}^{T_2} nC_P \frac{dT}{T} - nR \int_{P_1}^{P_2} \frac{dP}{P}$$

$$= nC_P \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

As the pressure is constant,

$$\Delta S_P = nC_P \ln \frac{T_2}{T_1}$$

Therefore,

$$n = \frac{200}{78} = 25.64 \text{ mol}$$

Now, entropy change in heating from 3°C to 5.7°C,

$$\Delta S_1 = 25.64 \text{ mol} \times 136.1 \text{ JK}^{-1} \text{ mol}^{-1} \ln \frac{278.7}{276} = 33.97 \text{ JK}^{-1}$$

Entropy change in melting,

$$\Delta S_2 = \frac{n\Delta_{\text{fusion}} H^\circ}{T_f} = \frac{9.87 \text{ kJ mol}^{-1}}{278.7 \text{ K}} \times 25.64 \text{ mol} = 908.03 \text{ JK}^{-1}$$

Entropy change in heating from 5.7°C to 80.3°C

$$\Delta S_3 = 25.64 \text{ mol} \times 136.1 \text{ JK}^{-1} \text{ mol}^{-1} \ln \frac{353.3}{278.7} = 827.7 \text{ JK}^{-1}$$

Entropy change in vaporization,

$$\Delta S_4 = \frac{n\Delta_{\text{vapour}} H^\circ}{T_b} = \frac{25.64 \text{ mol} \times 30.8 \times 10^3 \text{ J mol}^{-1}}{(273 + 80.3)\text{K}} = 2235 \text{ JK}^{-1}$$

Entropy change in heating from 80.3°C to 100°C,

$$\Delta S_5 = 25.64 \text{ mol} \times 136.1 \text{ JK}^{-1} \text{ mol}^{-1} \ln \frac{373}{353.3} = 192.3 \text{ JK}^{-1}$$

Therefore, total entropy change in heating 200 g benezene from 3°C to 100°C is

$$\begin{aligned} \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 &= 33.97 \text{ JK}^{-1} + 908.03 \text{ JK}^{-1} + 827.7 \text{ JK}^{-1} \\ &\quad + 2235 \text{ JK}^{-1} + 192.3 \text{ JK}^{-1} \\ &= 4197 \text{ JK}^{-1} \\ &= 4.197 \text{ kJK}^{-1} \quad \blacksquare \end{aligned}$$

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EXAMPLE 5.10 Methane gas (32 g) at 25°C expands isothermally from an initial pressure of 6×10^5 Nm^{-2} to a final pressure of 3×10^5 Nm^{-2}. Calculate the change in entropy of the gas.

Solution We have

$$n = \frac{32\text{ g}}{16\text{ g/mol}} = 2\text{ mol}$$

and

$$\Delta S = nC_P \ln\frac{T_2}{T_1} + nR \ln\frac{P_1}{P_2}$$

Therefore, for isothermal process, $T_1 = T_2$. Hence

$$\Delta S = nR \ln\frac{P_1}{P_2} = 2\text{ mol} \times 8.314\text{ JK}^{-1}\text{ mol}^{-1} \ln\frac{6\times10^5}{3\times10^5} = 11.53\text{ JK}^{-1} \quad \blacksquare$$

5.8 THE MAXWELL DEMON BOTTLE (MDB)

An assessment of this probability can be obtained using the device developed by Sussman[3] to provide answer to the general question of irreversibility in nature. Why is it that a burnt match stick does not unburn? Why do all of us grow older with time? Why is it extremely difficult to separate coffee and cream from a sample of cream coffee? Why is this unidirectionality? Let us focus our attention on the question of unmixing of coffee and cream from cream coffee. The Sussman's device which he calls as *Maxwell demon bottle* (MDB) is a closed bottle with a long neck and containing say 5 black balls (which are analogue of coffee) and say 5 white balls which are analogue of cream (Figure 5.5a). The bottle being closed disallows all mass transfer across the boundaries and hence makes the system a closed system.

Let us now invert the bottle so that all 5 black balls and all 5 white balls collect in the neck one over the other. If cream and coffee are to be separated from each other the configuration of the kind shown in Figure 5.5(b) should be obtained. Suppose the bottle is now brought back in the neck up position so that all the balls are drained off from the neck and come back in the body of the bottle and then again the bottle is put in the neck down position. The balls will again collect back in the neck but not necessarily in the configuration shown in Figure 5.5(b) (see Figure 5.5c). In order to have an idea of the probability of getting the same configuration as shown in Figure 5.5(b) we should know the total number of possible configurations. The total number of configurations (ω) is not difficult to calculate; it is equal to the number of ways of permuting 10 balls 5 of which are white and 5 of which are black, i.e.

$$\omega = \frac{10!}{5!5!} = 252 \tag{5.38}$$

which includes the configuration shown in Figure 5.5(b).

3. Scientific American, pp. 115–117, April 1973, Sussman, M.V., *Elementary General Thermodynamics*, Addison Wesley, 1972.

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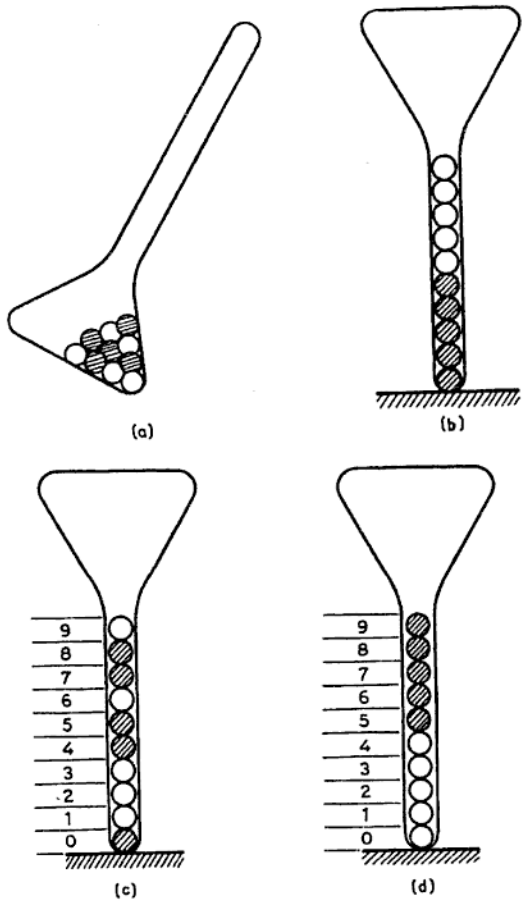

Figure 5.5 The Maxwell Demon Bottle (MDB): different complexions.

If all configurations are equally probable the probability of getting the configuration shown in Figure 5.5(b) is only 1 in 252, i.e. (1/252) which is quite meagre. In the actual sample of cream coffee the number of black balls and the number of white balls will be of the order of Avogadro number and therefore the value of ω will be astronomically a large figure and therefore the chances of getting the desired configuration of the type shown in Figure 5.5(b) will be negligibly small. This is why unmixing coffee and cream from the sample of cream coffee is difficult to the extent of being impossible.

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The arguments presented here can be extended to the case of energy conversion device shown in Figure 5.4(a) and to appreciate the point why it is not possible to have all the molecules of the gas in the desired configuration (Figure 5.4a) so that all of them strike perpendicularly at the piston to give us total conversion of heat into work. Thus the reason for the incomplete conversion of heat into work essentially lies in the statistics. It can be shown using Sussman's device that supply of heat to the system enhances indeterminacy.

In order to make the Sussman's device a thermodynamic device one should assign energy to it. In order to do that let us assume that black balls have unit mass each and white balls are massless spacers. The massless spacers (white balls) can be added to or withdrawn from the system. This is quite permissible because the Sussman's device is a closed system. If the bottle is supported in the neck down position as shown in Figure 5.5(c) with the top of the neck resting on the ground, we can assign a potential energy value to each black ball corresponding to its evaluation measured above the ground level. Thus we will assign an energy of zero units to the lowest position in the neck, an energy of 1 unit to the next higher position and so on. Let us call these as energy levels and assume that one energy level can have only one ball in it. The system will have the lowest energy (E_i) for the configuration shown in Figure 5.5(b) and will have the highest energy (E_f) for the configuration shown in Figure 5.5(d). That is,

$$E_i = 0 + 1 + 2 + 3 + 4 = 10 \text{ energy units} \tag{5.39}$$

$$E_f = 5 + 6 + 7 + 8 + 9 = 35 \text{ energy units} \tag{5.40}$$

If we call each of these configurations a quantum state, there are 252 quantum states, each having a definite energy, the lowest being 10 units and the highest being 35 units. The total energy E of the system would then be given by

$$E = E_1 + E_2 + \cdots + E_{252} \tag{5.41}$$

The average energy $\langle E \rangle$ of the system would then be given by

$$\langle E \rangle = \frac{1}{252} (E_1 + E_2 + \cdots + E_{252}) \tag{5.42}$$

If writing Equation (5.42) it has been assumed that all 252 quantum states are equally likely. We can generalize Equation (5.42) and write

$$\langle E \rangle = \sum_{n=1}^{n=252} P_n E_n \tag{5.43}$$

where P_n and E_n are the probability and energy of the nth quantum state respectively. Differentiation of Equation (5.43) gives

$$d\langle E \rangle = \sum E_n \, dP_n + \sum P_n \, dE_n \tag{5.44}$$

which says that the average energy of the system can be altered in two ways: (i) by changing P_n holding E_n constant and (ii) by changing E_n holding P_n constant. There is a striking similarity between Equation (5.44) and the well-known first law equation.

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$$dU = dQ_{\text{reversible}} + dW_{\text{reversible}} \tag{5.44a}$$

which says that the energy dU can be altered by energy transfer as heat and by energy transfer as work. Comparing Equations (5.44) and (5.44a), one would conclude that one of the terms on the right-hand side of Equation (5.44) should be the analogue of $dQ_{\text{reversible}}$ and the other should be the analogue of $dW_{\text{reversible}}$. The point to be decided now is that which term is analogue of which.

It can be seen that the work effect occurs when P's are held constant and E's are varied. This is easily accomplished by changing the elevation of the bottle. If the bottle is raised, as shown in Figure 5.6, the magnitude of each of the E_n's is increased without changing the P_n's; the work is done on the system. Thus $P_n\, dE_n$ is the analogue of dW_{rev}.

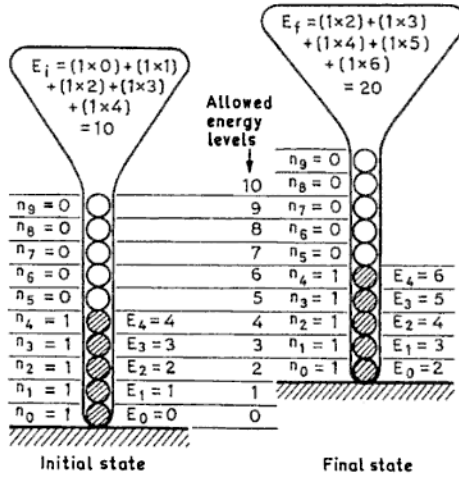

Figure 5.6 Work effects in MDB: n represents the number of balls and E represents the energy.

Similarly, it can be shown that $E_n\, dP_n$ is the analogue of $dQ_{\text{reversible}}$. To make the heat effects conspicuous let us consider that there are only 5 black balls in the bottle. The total number of configuration in this case is equal to 1. On addition of one white ball (massless spacer), the total number of configurations becomes

$$\frac{6!}{(5!)(1!)} = 6$$

when 2 white balls are added,

The total number of configurations becomes $\dfrac{7!}{(5!)(2!)} = 21$

Similarly when 3 white balls are added the total number of configurations becomes 56 and when 5 white balls are added the total number of configurations becomes

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252, and so on. The obvious result is that probability of finding any particular configuration decreases with addition of white balls. The addition of white balls makes it possible for individual black balls to climb higher into the neck of the bottle to higher energy levels. In addition to this, introduction of each white balls in the bottle introduces more and more indeterminacy. Therefore, adding white balls is the analogue of adding heat to the system. Thus, we can write from Equations (5.44) and (5.44a) that

$$\sum E_n \, dP_n = dQ_{\text{reversible}} \tag{5.45}$$

$$\sum P_n \, dE_n = dW_{\text{reversible}} \tag{5.46}$$

$$\langle E \rangle \equiv U \tag{5.47}$$

From Equation (5.45), it can be written that

$$\frac{dQ_{\text{reversible}}}{T} = dS = \sum_n \frac{E_n \, dP_n}{T} \tag{5.48}$$

Equation (5.48) makes clear the link between entropy and indeterminacy. It is, therefore, justified to write

$$S = f(\omega) \tag{5.49}$$

When a system is heated the randomness of the system increases and probability of finding the desired configuration (Figure 5.4a) decreases and this is why in the energy conversion devices like the one represented in Figure 5.4, complete conversion of disorganized energy to organized energy (mechanical work) is not possible. Entropy is a measure of the heat absorbed by the system which is unavailable for doing work.

EXAMPLE 5.11 Two black balls and one white ball, each of unit mass, are collected in the neck of an inverted Maxwell Demon bottle one over the other.

1. Calculate the total number of possible configurations.
2. If all configurations are equally probable then calculate probability of getting a configuration.
3. If one energy level can have only one ball and energy levels are 0, 1, 2... then calculate the total energy and average energy of the system.
4. If the lower level of the neck of the inverted bottle is raised one energy level up then calculate the change in the energy of the system.

Solution

1. Total number of possible configurations

$$\omega = \frac{3!}{(2!)(1!)} = \frac{3 \times 2}{2} = 3$$

Different configurations are BBO, BOB and OBB. B represents black ball and O represents white ball.

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2. Probability of getting a configuration = $\frac{1}{3}$

3. Total energy of the system

$$E = E_1 + E_2 + E_3 = (0 + 1 + 2) + (0 + 1 + 2) + (0 + 1 + 2) = 9$$

Therefore, average energy = $\frac{9}{3} = 3$

4. In this case,

total energy = $E_1' + E_2' + E_3' = (1+2+3)+(1+2+3)+(1+2+3) = 18$

Therefore, change in the total energy of the system = 18 − 9 = 9. ■

Entropy as an extensive property

The exact functional relationship between S and ω was given by Boltzmann who showed that

$$S = k \ln \omega \tag{5.50}$$

where k is the Boltzmann constant $k = R/N$, R being the gas constant and N being the Avagadro number. The relationship (5.50) and the extensive nature of entropy can be shown to be consistent with each other. Suppose two systems 1 and 2 have been combined to form the total system (1 + 2). Using Equation (5.50), we can write

$$S_1 = f(\omega_1); \qquad S_2 = f(\omega_2) \tag{5.51}$$

Since entropy is an extensive property, we can write

$$S_{1+2} = S_1 + S_2$$

or

$$f(\omega_{1+2}) = f(\omega_1) + f(\omega_2) \tag{5.52}$$

It is a well-known result from statistics that

$$\omega_{1+2} = \omega_1 \times \omega_2 \tag{5.53}$$

The relationship (5.53) can be proved in a very simple manner using Sussman's device. Consider two bottles 1 and 2 each having two black balls and one white ball. Each of the two systems will have $3!/(2!\,1!) = 3$ quantum states (see Figure 5.7a).

For total system (1 + 2) composed of the system 1 plus system 2 total number of quantum states would be 9, i.e. 3 × 3. This is illustrated in Figure 5.7(b). Of course the implied assumption is that all the quantum states in system 1 and in system 2 are equally probable.

From Equations (5.52) and (5.53), it follows that

$$f(\omega_1 \times \omega_2) = f(\omega_1) + f(\omega_2) \tag{5.54}$$

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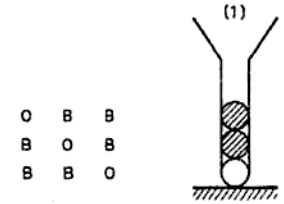
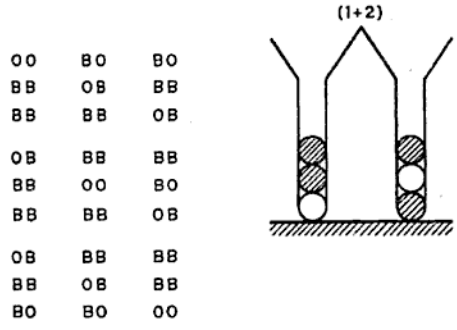


$$\text{Number of quantum states} = \frac{(2+1)!}{2!\,1!} = 3$$

$$S = k \ln 3$$

(a)



$$\text{Number of quantum states} = 3 \times 3 = 9$$

$$S_{(1+2)} = k \ln 3 \times 3 = 2 S_1$$

(b)

Figure 5.7 Demonstration of extensive nature of entropy.

which has the form

$$\ln (XY) = \ln X + \ln Y \tag{5.55}$$

Therefore, there is no alternative to the conclusion that the functional relationship between S and ω should be logarithmic in nature, i.e. Equation (5.50).

EXAMPLE 5.12 Calculate the relative number of distinguishable quantum states in 1 mol of water and ice at 273 K. Given $\Delta H_{\text{fusion}} = 6.0$ kJ mol^{-1} at 273 K and Boltzmann constant $k = 1.38 \times 10^{-23}$ JK^{-1}.

Solution We have

$$S_{\text{ice}} = k \ln \omega_{\text{ice}} \quad \text{and} \quad S_{\text{water}} = k \ln \omega_{\text{water}}$$

Then

$$S_{\text{water}} - S_{\text{ice}} = \Delta S = \frac{\Delta H_{\text{fusion}}}{T} = k \ln \frac{\omega_{\text{water}}}{\omega_{\text{ice}}}$$

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or

$$\frac{6000 \text{ J mol}^{-1}}{273 \text{ K}} = 2.303 \times 1.38 \times 10^{-23} \log \frac{\omega_{\text{water}}}{\omega_{\text{ice}}}$$

or

$$\frac{\omega_{\text{water}}}{\omega_{\text{ice}}} = 10^{6.9} \times 10^{23}$$

Thus, there are around 10^{24} times as many ways to arrange molecules in a mole of water in liquid as in ice. ■

5.9 THERMODYNAMIC DEFINITION OF TEMPERATURE AND PRESSURE

While dealing with Carnot's cycle we had attempted to give Kelvin's scale of temperature in terms of efficiencies of Carnot's engine. However, the main question remains that what should we understand by temperature in thermodynamic terms. The usual layman's concept of temperature is that it is a measure of the degree of hotness. When two bodies at different temperature are in contact, the cold body becomes hotter and the hot body becomes colder and ultimately the temperature of the two bodies become equal. That is, the heat flows from a higher temperature to a lower temperature and when the temperature equalize the heat does not flow. These empirical observations are not wrong but they must follow from a thermodynamic reasoning.

To do this, we will follow a simple approach. We will take two closed systems, each in thermodynamic equilibrium and put them in contact so that they interact with each other only in terms of energy transfer as heat and then look for the property which the two systems should have in common when the energy transfer as heat ceases. Let us consider a total system *C* which consists of two subsystems *A* and *B* separated from each other by a rigid wall which is thermally conducting but does not allow mass transfer across it. The total system *C* is an isolated system. The two subsystems *A* and *B* though individually in thermodynamic equilibrium are not in equilibrium with each other. The situation is depicted in Figure 5.8 which also indicates the direction of heat flow.

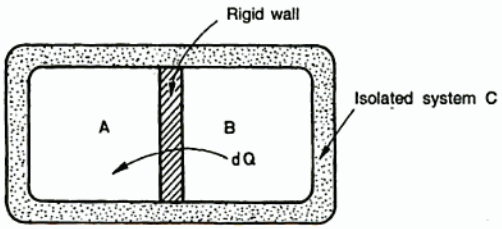

Figure 5.8 An isolated system consisting of two closed systems separated from each other by a thermally conducting rigid wall.

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For the system C, we can write the entropy (S_C) of the total system in terms of entropies of subsystems A and B, i.e.

$$S_C = S_A + S_B \tag{5.56}$$

Since entropy is a state function, $S = S(U, V)$, we can rewrite Equation (5.56) as

$$S_C = S_A(U_A, V_A) + S_B(U_B, V_B) \tag{5.57}$$

Since the total system C is isolated its entropy cannot decrease and since the wall between the subsystems A and B is rigid interaction between A and B cannot be in terms of energy transfer as work—it can only be in terms of energy transfer as heat. As a result of this interaction, the total internal energy

$$U_C = U_A + U_B = \text{constant} \tag{5.58}$$

which although remains constant for the isolated system C is shared by the two subsystems A and B. If r represents the fraction of the total internal energy shared by A, we can write

$$U_A = rU_C; \quad U_B = (1-r)U_C \tag{5.59}$$

In view of the facts that the total system C is an isolated system and the wall separating the subsystems A and B is a rigid wall, U_C, V_A and V_B would remain constant. The only parameter which may vary during the course of interaction between A and B is r. When the systems A and B attain thermal equilibrium with each other the value of S_C should attain its maximum. The condition of maximum can be written as

$$\frac{dS_C}{dr} = 0 \tag{5.60}$$

From Equations (5.57) and (5.59), we have

$$\begin{aligned} \frac{dS_C}{dr} &= \left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} \frac{dU_A}{dr} + \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} \frac{dU_B}{dr} \\ &= \left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} U_C + \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} (-U_C) \end{aligned} \tag{5.61}$$

From Equations (5.60) and (5.61), it follows that at thermal equilibrium between A and B

$$\left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} = \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} \tag{5.62}$$

Thus $(\partial S/\partial U)_V$ is the property which the two systems A and B should have in common when thermal equilibrium is attained. Dimensional analysis will show that $(\partial S/\partial U)$ has the dimensions of temperature^{-1} (S = energy/temperature and U = energy). Therefore,

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$$T \equiv \frac{1}{(\partial S/\partial U)_V} \tag{5.63}$$

Equation (5.63) gives us thermodynamic definition of temperature.

We can also establish the direction of heat flow using Equation (5.61) from which it follows that

$$dS_C = U_C d_r \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \tag{5.64}$$

Since $T_B \neq T_A$ initially and $dS_C > 0$ for the total isolated system it follows that $dr > 0$, $T_B > T_A$. This means that when $T_B > T_A$, U_A increases and U_B decreases, i.e. the heat flows from B to A.

Let us take this analysis a little further to learn more about the relationship between T and U. Since $dS_C/dr = 0$ represents the condition of a maximum, the second derivation, i.e. d^2S_C/dr^2 should be negative. Hence from Equation (5.61), we can write

$$\frac{d^2S_C}{dr^2} = \left(\frac{\partial^2 S_A}{\partial U_A^2}\right)_{V_A} U_C^2 + \left(\frac{\partial^2 S_B}{\partial U_B^2}\right)_{V_B} U_C^2 < 0 \tag{5.65}$$

If A and B are identical systems, we get from Equation (5.65)

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V < 0 \qquad \text{for } A \text{ and } B \tag{5.66}$$

or

$$\left(\frac{\partial T}{\partial U}\right)_V > 0 \tag{5.67}$$

That means temperature must be a monotonically increasing function of internal energy at fixed volume.

Pressure

Pressure in mechanics is the force per unit area. In terms of atoms and molecules, the pressure exerted by a gas is understood in terms of molecular collisions with the boundary walls of the systems. These definitions are certainly not thermodynamic definitions. In this section, we will proceed in the manner, similar to what we did in the case of temperature and arrive at a thermodynamic definition of pressure and then show the correspondence between thermodynamic pressure and mechanical pressure.

Consider once again an isolated system which consists of two subsystems A and B separated from each other by a wall (Figure 5.9). The wall this time is not rigid; it is a flexible wall which is impermeable to mass but is permeable to heat.

The systems A and B would naturally interact with each other in terms of both energy transfer as heat and energy transfer as work. The system C being an isolated system gives

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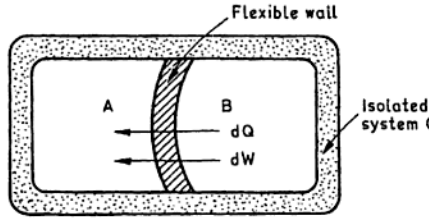

Figure 5.9 An isolated system consisting of two closed systems separated from each other by a thermally conducting and flexible wall.

$$U_C = U_A + U_B = \text{constant} \tag{5.68}$$

and

$$V_C = V_A + V_B = \text{constant} \tag{5.69}$$

As a result of interactions between A and B, U_C and V_C will be shared between A and B. Thus

$$U_A = r_U U_C; \qquad U_B = (1 - r_U) U_C \tag{5.70}$$

and

$$V_A = r_V V_C; \quad V_B = (1 - r_V) V_C \tag{5.71}$$

Where r_U is fraction of the total internal energy shared by A and r_V has a similar meaning for volume. For the isolated system C, the equilibrium state would be the state of maximum entropy and given by the conditions

$$\left(\frac{\partial S_C}{\partial r_U}\right)_{r_V} = 0; \quad \left(\frac{\partial S_C}{\partial r_V}\right)_{r_U} = 0 \tag{5.72}$$

In view of Equation (5.57) which is valid in this case also and from Equations (5.70) and (5.71) the conditions (5.72) yield

$$\left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} U_C - \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} U_C = 0 \tag{5.73}$$

and

$$\left(\frac{\partial S_A}{\partial V_A}\right)_{U_A} V_C - \left(\frac{\partial S_B}{\partial V_B}\right)_{U_B} V_C = 0 \tag{5.74}$$

In a system like the one considered here both thermal and mechanical equilibrium would prevail. The condition (5.73) as shown already is the condition of thermal equilibrium $T_A = T_B$. Hence the condition (5.74) should represent the condition of mechanical equilibrium. Dimensional analysis reveals that the derivative $(\partial S/\partial V)$ has the dimensions of P/T; S has the dimensions of

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$$\frac{\text{Energy}}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}}$$

and V has the dimensions of (length)^3. From Equation (5.74), it follows that at $T_A = T_B$,

$$\left(\frac{\partial S_C}{\partial r_V}\right)_{\eta} = \left[\left(\frac{\partial S_A}{\partial V_A}\right)_{U_A} - \left(\frac{\partial S_B}{\partial V_B}\right)_{U_B}\right] V_C \geq 0$$

or

$$dS_C = \left[\left(\frac{\partial S_A}{\partial V_A}\right)_{U_A} - \left(\frac{\partial S_B}{\partial V_B}\right)_{U_B}\right] V_C \, dr_V \geq 0 \tag{5.75}$$

The equality holds at equilibrium and the inequality at non-equilibrium situation. Let us bear in mind that the entropy of an isolated system cannot decrease; it increases with time and then stabilizes at a maximum value when equilibrium is reached. If $dr_V > 0$, i.e. the subsystem A expands and V_C has to be positive because negative volume has no meaning, it follows from Equation (5.75) that at $T_A = T_B$. $P_A > P_B$ at a non-equilibrium state, and $P_A = P_B$ at equilibrium state. Thus the thermodynamic definition of pressure is given by

$$\frac{P}{T} \equiv \left(\frac{\partial S}{\partial V}\right)_U \tag{5.76}$$

Under what conditions the thermodynamic pressure equals the mechanical pressure would become clear by the following argument. We know that

$$dS - \frac{dQ}{T} \geq 0 \tag{5.77}$$

the equality holds for reversible process and the inequality holds for irreversible process. Writing $S = S(U, V)$ and utilizing thermodynamic definition of pressure and temperature, i.e. Equations (5.76) and (5.63)

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \quad \text{or} \quad dS = \frac{1}{T} dU + \frac{P}{T} dV \tag{5.78}$$

In Equation (5.78) P and T are thermodynamic pressure and temperature, respectively. Now from the first law for the situation where mechanical work is the only work mode, we can write

$$dQ + dW = dU \quad \text{or} \quad dQ - P_m \, dV = dU \tag{5.79}$$

where P_m is the mechanical pressure. Substituting values of dS and dQ from Equations (5.78) and (5.79) in Equation (5.77), we have

$$\frac{dU}{T} + \frac{P}{T} dV - \left(\frac{dU}{T} + \frac{P_m}{T} dV\right) \geq 0 \quad \text{or} \quad (P - P_m) dV \geq 0 \tag{5.80}$$

It is easy to see from Equation (5.80) that for expansion where $dV > 0$,

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$$P = P_m, \quad \text{for reversible process} \tag{5.81}$$

and

$$P > P_m, \quad \text{for irreversible process} \tag{5.82}$$

Similarly for the contraction process

$$P = P_m, \quad \text{for reversible process} \tag{5.83a}$$

and

$$P < P_m, \quad \text{for irreversible process} \tag{5.83b}$$

5.10 COMBINING FIRST AND SECOND LAWS OF THERMODYNAMICS

The first law statement is written as

$$dQ + dW = dU$$

If dQ is the heat added to the system reversibly and dW is the mechanical work done reversibly on the system, the first law statement can be rewritten as

$$dU = T\,dS - P\,dV \tag{5.84}$$

where $dQ/T = dS$. Similarly utilizing both first and second laws we can deduce a relationship between enthalpy H and entropy S:

$$H = U + PV$$

or

$$dH = dU + P\,dV + V\,dP = dQ + V\,dP \tag{5.85}$$

or

$$dH = T\,dS + V\,dP$$

5.11 THE FREE ENERGY AND WORK FUNCTIONS

So far we have derived the following conditions of equilibrium:

$$(dS)_{U,V} = 0 \tag{5.86}$$

and

$$(dU)_{S,V} = 0 \tag{5.87}$$

The first condition represents the conditions of a maximum and the second one represents the condition of a minimum. That is at constant U and V, entropy has a tendency to maximize and at constant S and V, U has a tendency to minimize. What happens when U and S are forced to strike a compromise. Constant U and V or constant S and V are not the usual conditions under which most processes are carried out. Constant temperature and pressure or constant temperature and volume are the conditions under which a vast category of chemical and physico-chemical processes are carried out and hence it is desirable to deduce the conditions of equilibrium for these situations.

For changes at constant temperature along a reversible path we know $dQ = T\,dS$ which when substituted in the first law equation yields

$$dU = T\,dS + dW_{\text{reversible}} \tag{5.88}$$

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where $dW_{\text{reversible}}$ is the reversible work done on the system. Any system satisfying Equation (5.88) should in fact be in equilibrium. This is because every point in a reversible path is an equilibrium point; the reversible path traverses a succession of equilibrium states. If temperature T = constant, Equation (5.88) can be rewritten in the form

$$d(U - TS) = dW_{\text{reversible}} \tag{5.89}$$

Equation (5.89) leads us to the definition of a new function A given by

$$A = U - TS \tag{5.90}$$

Such that

$$dA = dW_{\text{reversible}} \qquad \text{at } T = \text{constant} \tag{5.91}$$

It is obvious that if work done on the system is irreversible

$$dA < dW_{\text{irreversible}} \text{ at } T = \text{constant} \tag{5.92}$$

If P-V work is the only work permissible then it follows from Equation (5.91)

$$dA = -P\,dV \tag{5.93}$$

If in addition to constant temperature condition constant volume condition is also imposed on the system

$$(dA)_{T,V} = 0 \tag{5.94}$$

Since U has a tendency to minimize and S has a tendency to maximize as the system approaches equilibrium, a perusal of Equation (5.90) reveals that Equation (5.94) should represent the condition of a minimum. Thus, we arrive at a new condition of equilibrium at constant T and V; the work function A is minimum at equilibrium. This condition of equilibrium should be applicable to the chemical processes going on in a bomb calorimeter. The function A is called *work function* or *Helmholts free energy*.

Now let us deduce the condition of equilibrium for processes going on at constant T and P (usually known as *table-top conditions*). We know that

$$H = U + PV$$

or

$$\begin{aligned} dH &= dU + P\,dV + V\,dP \\ &= T\,dS + dW_{\text{reversible}} + P\,dV + V\,dP \end{aligned} \tag{5.95}$$

If T and P are held constant we get from Equation (5.95)

$$d(H - TS) = dW_{\text{reversible}} + P\,dV \tag{5.96}$$

Defining the new function

$$G = H - TS \tag{5.97}$$

We can rewrite Equation (5.96) as

$$(dG)_{T,P} = dW_{\text{reversible}} + P\,dV \tag{5.98}$$

If P-V work is the only permitted work $dW_{\text{reversible}} = -P\,dV$ and therefore from Equation (5.98) it follows that

$$(dG)_{T,P} = 0 \tag{5.99}$$

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By the same logic as followed in the case of work function A, it can be shown that Equation (5.99) represents the condition of a minimum. Thus, we have arrived at a new condition of equilibrium. At constant T and P when only P-V work is permitted G attains a minimum at equilibrium. This equilibrium condition is most useful under ordinary laboratory conditions. The function G is called the Gibb's free energy.

Thus, we have arrived at four conditions of equilibrium:

$$(dS)_{U,V} = 0 \tag{5.100}$$

$$(dU)_{S,V} = 0 \tag{5.101}$$

$$(dA)_{T,V} = 0 \tag{5.102}$$

$$(dG)_{T,P} = 0 \tag{5.103}$$

The first one represents the condition of maxima and the remaining three represent the conditions of minima.

5.12 MAXWELL'S RELATIONS

U, H, A and G are all state functions and are given by equations

$$dU = T\,dS - P\,dV \tag{5.84}$$

$$dH = T\,dS + V\,dP \tag{5.85}$$

$$dA = dU - T\,dS - S\,dT = -P\,dV - S\,dT \tag{5.104}$$

$$dG = dH - T\,dS - S\,dT = dU + P\,dV + V\,dP - T\,dS - S\,dT$$

or

$$dG = V\,dP - S\,dT \tag{5.105}$$

Since U, H, A and G are all state functions, Equations (5.84), (5.85), (5.104) and (5.105) should be exact differential equations of the form

$$df = M\,dx + N\,dy, \qquad \text{where } f = f(x, y)$$

and hence the Euler's reciprocity relations

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

should be obeyed. Hence it follows that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{5.106a}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{5.106b}$$

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$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{5.106c}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{5.106d}$$

Equations (5.106a)–(5.106d) are well-known Maxwell's relations and are very helpful in deducing a number of thermodynamic relationships. This will be illustrated a short while from now.

EXAMPLE 5.13 Four moles of an ideal gas are compressed isothermally at 300 K from 2.02×10^5 N m^{-2} 4.04×10^5 N m^{-2}. Calculate the value of ΔG (Given $R = 8.314$ JK^{-1} mol^{-1}).

Solution We have $dG = V\,dP - S\,dT$. When temperature is constant, $dT = 0$. Then

$$(dG)_T = V\,dP = \frac{nRT}{P}dP$$

or

$$\Delta G = \int_1^2 \frac{nRT}{P}dP = nRT \ln\frac{P_2}{P_1}$$

$$= 4 \times 8.314 \times 300 \times 2.303 \log\frac{4.04 \times 10^5}{2.02 \times 10^5}$$

$$= 6916.6 \text{ J} \quad \blacksquare$$

EXAMPLE 5.14 One mole of an ideal gas expands isothermally and reversibly at 27°C from a volume of 2 m^3 to 20 m^3. Calculate ΔA for the process (when $R = 8.314$ JK^{-1} mol^{-1}).

Solution As $dA = -P\,dV - S\,dT$. Since $dT = 0$, we have

$$(dA)_T = -P\,dV = -nRT\frac{dV}{V}$$

or

$$\Delta A = \int_1^2 -nRT\frac{dV}{V}$$

$$= -nRT \ln\frac{V_2}{V_1}$$

$$= -1 \times 8.314 \times (27 + 273) \times 2.303 \log\frac{20}{2}$$

$$= -5744 \text{ J mol}^{-1} \quad \blacksquare$$

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EXAMPLE 5.15 For the following combustion reaction

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

performed in a bomb calorimeter $\Delta S^\circ = 182.45\ JK^{-1}\ mol^{-1}$ at 25°C and $\Delta U^\circ = -2808$ kJ mol^{-1} at 25°C; calculate the energy change that can be extracted as (a) heat and (b) work. Also calculate ΔH°.

Solution The reaction is taking place in a bomb calorimeter means that there is no change in the volume of the container. Since expansion work = 0, $\Delta U = Q$ at constant volume. Therefore, $Q = -2808$ kJ mol^{-1}

1. Since 2808 kJ mol^{-1} energy can be extracted as heat,

   $\Delta A = \Delta U - T\Delta S$

   $= (-2808 - 298 \times 182.4 \times 10^{-3})\ kJmol^{-1}$

   $= -2862\ kJ\ mol^{-1}$

   $\Delta A = +W_{maximum}$ ($\Delta A = \Delta U - T\Delta S = \Delta U - Q_{reversible}$, $\Delta A = +W_{maximum}$)

   $W_{maximum} = -2862\ kJ\ mol^{-1}$
2. 2862 kJ mol^{-1} energy can be extracted as maximum work.
3. We know $\Delta H^\circ = \Delta U^\circ + \Delta nRT$, here $\Delta n = 6 - 6 = 0$. Therefore, $\Delta H^\circ = \Delta U^\circ = -2808\ kJ\ mol^{-1}$. ■

EXAMPLE 5.16 For the following combustion reaction

$$C_8H_{18}(g) + 12.5O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$

performed in a bomb calorimeter $\Delta S = 421.5\ JK^{-1}$ at 25°C and heat of the reaction at 25°C = −5109000 J. Calculate both ΔA and ΔG for the reaction.

Solution Since we know

$$\Delta A = \Delta U - T\Delta S$$
$$= 5109000 - (273+25)(421.5)$$
$$= -5234600\ J$$

and

$$G = H - TS = A + PV$$

Then

$$dG = dA + d(PV) \quad \text{or} \quad \Delta G = \Delta A + \Delta(PV)$$

For a perfect gas

$$\Delta(PV) = (\Delta n)RT$$

Hence

$$\Delta G = \Delta A + (\Delta n)RT$$

where

$\Delta n = 8 - 13.5 = -5.5$

$\Delta G = -5234600 + (-5.5) \times 8.314 \times (273 + 25) = -5248227\ J$ ■

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EXAMPLE 5.17 The standard entropy change for the following combustion reaction

$$C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$$

is $\Delta S° = -339.23\ JK^{-1}$ at 25°C. Calculate ΔA and ΔG of the reaction if

$$\Delta_f H°(C_3H_6, g) = 20.42\ kJ\ mol^{-1}$$

$$\Delta_f H°(CO_2, g) = -393.51\ kJ\ mol^{-1}$$

$$\Delta_f H°(H_2O, l) = -285.83\ kJ\ mol^{-1}$$

Solution We have

$$\Delta H° = 3\times\Delta_f H°(CO_2, g) + 3\times\Delta_f H°(H_2O, l) - \left[\Delta_f H°(C_3H_6, g) + \frac{9}{2}\times\Delta_f H°(O_2, g)\right]$$

$$= 3\times(-393.51) + 3\times(-285.83) - \left(20.42 + \frac{9}{2}\times 0\right)$$

$$= -1180.53 - 857.49 - 20.42$$

$$= -2058.44\ kJ$$

We also have

$$\Delta H = \Delta U + (\Delta n)RT$$

where

$$\Delta n = 3 - 1 - \frac{9}{2} = \frac{6-2-9}{2} = \frac{6-11}{2} = -\frac{5}{2}$$

Then

$$\Delta U = \Delta H - (\Delta n)RT$$

$$= -2058.44\ kJ - \left(-\frac{5}{2}\right)mol \times 8.314\times10^{-3}\ kJ\ K^{-1}\ mol^{-1} \times 298\ K$$

$$= (-2058.44 + 6.19)\ kJ$$

$$= -2052.25\ kJ$$

Hence

$$\Delta A = \Delta U - T\Delta S$$

$$= \left(-2052.25 - 298\times(-339.23)\times10^{-3}\right)\ kJ$$

$$= (-2052.25 + 101.09)\ kJ$$

$$= -1951.16\ kJ$$

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and

$$\Delta G = \Delta A + (\Delta n)RT$$
$$= -1951.16 \text{ kJ} + \left(-\frac{5}{2}\right) \times 8.314 \times 10^{-3} \times 298 \text{ kJ}$$
$$= (-1951.16 - 6.19) \text{ kJ}$$
$$= -1957.35 \text{ kJ} \quad \blacksquare$$

5.13 GIBBS–HELMHOLTZ EQUATION

We know that $G = H - TS$ and $dG = -S\,dT + V\,dP$. Therefore,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{5.107a}$$

Similarly, for the work function $A = U - TS$ and $dA = -P\,dV - S\,dT$. Therefore,

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \tag{5.107b}$$

Combining Equation (5.97) with (5.107a), we get

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \tag{5.108a}$$

The difference form of this equation would obviously be

$$\Delta G = \Delta H + T\left(\frac{\partial (\Delta G)}{\partial T}\right)_P \tag{5.108b}$$

or

$$\left[\frac{\partial (\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2} \tag{5.108c}$$

or

$$\left[\frac{\partial (\Delta G/T)}{\partial (1/T)}\right]_P = \Delta H \tag{5.108d}$$

Similarly combining Equations (5.90) and (5.107b), we can write for the work function

$$A = U + T\left(\frac{\partial A}{\partial T}\right)_V \tag{5.109a}$$

the difference form of which would be

$$\Delta A = \Delta U + T\left[\frac{\partial (\Delta A)}{\partial T}\right]_V \tag{5.109b}$$

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or

$$\left[\frac{\partial(\Delta A/T)}{\partial T}\right]_V = -\frac{\Delta U}{T^2} \tag{5.109c}$$

or

$$\left[\frac{\partial(\Delta A/T)}{\partial(1/T)}\right]_V = \Delta U \tag{5.109d}$$

Equations (5.108) and (5.109) are called the *Gibbs–Helmholtz equations* and are quite helpful in thermodynamic computation. For example, these equations give us a way for calculating free energy changes from thermal data (say, heat of the process).

EXAMPLE 5.18 Prove that,

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T^2} \quad \text{and} \quad \left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T_2}$$

Solution We have

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -G\frac{1}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P \tag{1}$$

where

$$dG = V\,dP - S\,dT$$

and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{2}$$

Then from Equation (1), we get

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{G}{T^2} - \frac{S}{T} = \frac{-1}{T^2}(G + ST) \tag{3}$$

where

$$G = H - TS \quad \text{or} \quad H = G + TS$$

From Equation (2), we have

$$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T_2}$$

Now

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{A}{T^2} + \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V \tag{4}$$

where

$$dA = -P\,dV - S\,dT \quad \text{and} \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

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From Equation (4), we obtain

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{A}{T^2} - \frac{S}{T} = -\frac{1}{T^2}(A + ST) \tag{5}$$

where

$$A = U - TS \quad \text{or} \quad A + TS = U$$

From Equation (5), we get

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T^2} \qquad \blacksquare$$

5.14 FREE ENERGY AND THE EFFICIENCY OF ENERGY CONVERSION

Just from the very definitions of G and A, it is easy to see that

$$dG = dA + P\,dV \tag{5.110}$$

We have also shown earlier that

$$dA = dW_{\text{reversible}} \tag{5.91}$$

where $dW_{\text{reversible}}$ is the work done on the system. Hence it would follow that

$$-dA = -dW_{\text{reversible}} \tag{5.111}$$

which would mean that decrease in the work function A is a measure of the reversible work obtainable from the system. Thus rewriting Equation (5.110), we get

$$\underset{\text{(Decrease in } G)}{-dG} = \underset{\left(\begin{array}{c}\text{Reversible work}\\ \text{done by the system}\end{array}\right)}{-dW_{\text{reversible}}} - \underset{\left(\begin{array}{c}\text{Pressure volume, i.e.}\\ \text{mechanical work done}\\ \text{by the system}\end{array}\right)}{(P\,dV)} \tag{5.112}$$

We conclude that the decrease in Gibbs free energy is a measure of the net reversible work obtainable from the system. By the term 'net work' we mean all kinds of work excluding pressure–volume work (mechanical work). Thus the decrease in Gibbs free energy is equal to the amount of maximum work which a system can do at constant temperature and pressure over and above the mechanical work, i.e. non-expansion work.

The efficiency of energy conversion (e) can be written as

$$e = \frac{\text{Net work obtained}}{\text{Total energy}} = \frac{\Delta G}{\Delta H}$$

Since $\Delta G = \Delta H - T\Delta S$,

$$e = 1 - \frac{T\Delta S}{\Delta H} \tag{5.113}$$

As $\Delta S > 0$ for spontaneous process, it is easy to see that e is always less than one. The efficiency e can be equal to unity when either $T = 0$ or $\Delta S = 0$; the unattainability of absolute zero of temperature by finite number of operations (third law) has already been indicated while discussing Carnot's engine. Thus

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$T\Delta S$ is a measure of unavailable energy; unavailable for doing organized work. This makes clear why ΔG is called free energy. It is free or available for doing work. Similar considerations would apply to work function A (Helmholtz free energy).

5.15 SPONTANEOUS CHANGES IN A SYSTEM

We know that $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. For spontaneous process $\Delta S_{\text{total}} > 0$. Now if ΔH is the change in enthalpy of the system at constant temperature and pressure. Then the change in entropy of surroundings

$$\Delta_{\text{surroundings}} = -\frac{\Delta H}{T}$$

But, when exothermic process ΔH is negative, therefore $\Delta S_{\text{surroundings}}$ is positive. Therefore

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H}{T}$$

or

$$-T\Delta S_{\text{total}} = \Delta H - T\Delta S_{\text{system}}$$

Therefore,

$$-T\Delta S_{\text{total}} = \Delta G = \Delta H - T\Delta S_{\text{system}}$$

Since ΔS_{total} is positive for a spontaneous process. Therefore, for a spontaneous process ΔG is negative. Remember that for a spontaneous process ΔS_{system} may be negative but ($\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$) must be positive.

EXAMPLE 5.19 Standard entropy change for the combustion reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

at constant pressure and temperature (25°C) is –242.98 JK^{-1}. Calculate the total entropy change using following data:

$$\Delta_f H^\circ(CH_4, g) = -74.81 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(CO_2, g) = -393.51 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(H_2O, l) = -285.83 \text{ kJ mol}^{-1}$$

Solution We have

$$\begin{aligned}\Delta H &= \Delta_f H^\circ(CO_2, g) + 2\times\Delta_f H^\circ(H_2O, l) - \left[\Delta_f H^\circ(CH_4, g) + 2\times\Delta_f H^\circ(O_2, g)\right] \\ &= -393.51 + 2\times(-285.83) - (-74.81) \\ &= -965.17 + 74.81 \\ &= -890.36 \text{ kJ} \quad \blacksquare\end{aligned}$$

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where

$$\Delta S_{\text{system}} = -242.98 \text{ JK}^{-1}$$

and

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T} = -\frac{-890.36\times10^{3} \text{ JK}^{-1}}{298} = 2988 \text{ JK}^{-1}$$

Therefore,

$$S_{\text{total}} = (-242.98 + 2988) \text{ JK}^{-1} = 2.75 \text{ k JK}^{-1}$$

Although ΔS_{system} is negative, but ΔS_{total} is positive, therefore the combustion reaction is spontaneous.

EXAMPLE 5.20 The standard heat of formation of H_2O (l) from its element is –285.83 kJ mol^{-1} and standard entropy change for the same reaction is –327 JK^{-1} at 25°C. Will the reaction be spontaneous at 25°C?

Solution We have

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

where

$$\Delta H = 2\Delta_f H^{\circ}(H_2O, l) - 0 - 0 = 2(-285.83) \text{ kJ} = -571.66 \text{ kJ}$$

and

$$\Delta S = -327 \text{ JK}^{-1}$$

Then

$$\Delta G = \Delta H - T\Delta S = -571.66 \text{ kJ} - 298\left(-327\times10^{-3}\right) \text{ kJ}$$

$$= -571.66 \text{ kJ} + 97.45 \text{ kJ}$$

$$= -474.21 \text{ kJ}$$

Here ΔG is negative. Therefore, the reaction is spontaneous. ■

5.16 STANDARD GIBBS FREE ENERGY OF FORMATION

Standard Gibbs free energy of formation, ΔG_f°, of a compounds is the free energy change for the formation of one mole of compound from its elements in their reference state when all the reactants and products are present in their standard state (pure, 1 bar). For example

$$C(\text{s, graphite}) + O_2(g) \rightarrow CO_2(g), \quad \Delta G_f^{\circ} = -394.36 \text{ kJ mol}^{-1}$$

Therefore, standard reaction Gibbs energy $\Delta_r G^{\circ}$ can be written as

$$\Delta_r G^{\circ} = \sum_{\text{products}} n\Delta G_f^{\circ}(\text{products}) - \sum_{\text{reactants}} n\Delta G_f^{\circ}(\text{reactants})$$

The standard Gibbs energy of formation of some compounds at 25°C are shown in Table 5.1.

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Table 5.1 Standard Gibbs Energy of Formation of Some Compounds

Compounds	ΔG_f°/kJ mol^{-1}
CO_2 (g)	−394.36
CH_4 (g)	−50.72
C_6H_6 (l)	+124.30
$C_6H_{12}O_6$ (s)	−910.00
H_2O (l)	−237.13
NH_3 (g)	−16.45
NaCl (s)	−384.14

EXAMPLE 5.21 The standard entropy change $\Delta_r S^\circ$ for

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

is $-242.98\ JK^{-1}$ at 25°C. Calculate the standard reaction enthalpy for the above reaction if standard Gibbs energy of formation of CH_4 (g), CO_2 (g) and H_2O (l) are −50.72, −394.36 and −237.13 kJ mol^{-1}, respectively.

Solution Here

$$\Delta_r G^\circ = \Delta G_f^\circ(CO_2, g) + 2\Delta G_f^\circ(H_2O, l) - \left[\Delta G_f^\circ(CH_4, g) + 2\Delta G_f^\circ(O_2, g)\right]$$

$$= -394.36 + 2(-237.13) - (-50.72 + 0)$$

$$= -868.62 + 50.72$$

$$= -817.9\ kJ$$

and

$$\Delta_r S^\circ = -242.98\ JK^{-1} = -242.98 \times 10^{-3}\ kJK^{-1}$$

We also have

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

or

$$\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ = -817.9\ kJ + 298\ K\left(-242.98 \times 10^{-3}\right) kJK^{-1}$$

$$= -817.9 - 72.41$$

$$= -890.31\ kJ \quad \blacksquare$$

EXAMPLE 5.22 What is the maximum energy that can be extracted as non-expansion work for the combustion of 25 g of glucose under the standard condition at 25°C when the reaction is

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

and the standard Gibbs energy of formation of

$C_6H_{12}O_6$ (s), CO_2 (g) and H_2O (l) are −910 kJ mol^{-1}, −394.4 kJ mol^{-1} and −237.13 kJmol^{-1}, respectively?

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Solution Maximum energy that can be extracted as non-expansion work is equal to the change in free energy of the system. Therefore,

$$\begin{aligned}\Delta_r G^\circ &= 6\times\Delta G_f^\circ\left(CO_2, g\right) + 6\times\Delta G_f^\circ\left(H_2O, l\right)\\ &\quad -\left[\Delta G_f^\circ\left(C_6H_{12}O_6, s\right) + 6\times\Delta G_f^\circ\left(O_2, g\right)\right]\\ &= 6\times(-394.4)+6(-237.13)-[-910+0]\\ &= (-2366.4-1422.78+910) = -2879.18 \text{ kJ mol}^{-1}\end{aligned}$$

Now

$$25 \text{ g of glucose} = \frac{25}{180.2} = 0.139 \text{ mol}$$

Therefore, Gibbs free energy change for the combustion of 0.139 mol of glucose = -2879.18×0.139 kJ = -400.2 kJ. Thus, 400.2 kJ energy can be extracted as non-expansion work. ■

5.17 APPLICATIONS OF MAXWELL'S RELATIONS

Here we will give one example where Maxwell's relations are used with advantage to deduce thermodynamic correlations.

Thermodynamic equation of state

Combining the first and the second laws, we have

$$T\,dS = dU + P\,dV$$

or

$$P = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial U}{\partial V}\right)_T \tag{5.114}$$

Using Maxwell's relation (5.106c) we can rewrite Equation (5.114) as

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{5.115}$$

Equation (5.115) is called *thermodynamic equation of state.*

For an ideal gas ($PV = nRT$) it follows from Equation (5.115) that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{5.116}$$

which means that for an ideal gas, U is a function of T only, i.e. $U = U(T)$. This result as mentioned in Chapter 3 was first arrived at by Joule through an experiment whose design was faulty. Though Joule made this statement, Equation (5.116), for all gases, it is true only for ideal gases. The quantity $\partial U/\partial V$ has

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the dimension of pressure and is called *internal pressure* of a gas. The fact that internal pressure is zero is consistent with the assumption that there are no intermolecular forces in ideal gases.

Starting with equation

$$dH = T\,dS + V\,dP$$

and using Maxwell's relation one can also deduce that

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{5.117}$$

Equation (5.117) is also called *thermodynamic equation of state*. For an ideal gas it also follows from Equation (5.117) that

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \tag{5.118}$$

which implies that for an ideal gas it is a function of T only, i.e. $H = H(T)$.

5.18 JOULE–THOMSON COEFFICIENT OF A REAL GAS

We have already shown that the Joule–Thomson coefficient μ_{JT} is given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \tag{3.36}$$

In view of Equation (5.117), Equation (3.36) can be rewritten as

$$\mu_{JT} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \tag{5.119}$$

For an ideal gas, it is obvious from Equation (5.119) that $\mu_{JT} = 0$. However, for a real (non-ideal) gas it may not be so. Let us calculate the value of μ_{JT} for a van der Waals, gas obeying equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = nRT \tag{5.120}$$

where a and b are van der Waals, constants. For one mole of van der Waals, gas, we can write

$$PV = RT + Pb - \frac{a(V-b)}{V^2}$$

or

$$V = \frac{RT}{P} + b - \frac{a}{PV} + \frac{ab}{PV^2} \tag{5.121}$$

As a first approximation V may be replaced by RT/P in the correction term $a/(PV)$ and $ab/(PV^2)$ so that

$$V = \left(\frac{RT}{P}\right) + b - \frac{a}{RT} + \frac{abP}{R^2T^2} \tag{5.122}$$

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Differentiation of Equation (5.122) with respect to temperature at constant pressure yields

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3} = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{2abP}{R^2T^3} \tag{5.123}$$

Using Equation (5.123) in Equation (5.119), we get

$$\mu_{JT} = \frac{1}{C_P}\left(\frac{2a}{RT} - b - \frac{3abP}{R^2T^2}\right) \tag{5.124}$$

At a very low pressure, the last term in the brackets becomes negligible and therefore Equation (5.124) reduces to

$$\mu_{JT} = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right) \tag{5.125}$$

Equation (5.125) gives the expression for Joule–Thomson coefficient for a van der Walls' gas. The value of inversion temperature T_i can be obtained by putting $\mu_{JT} = 0$. Thus

$$T_i = \frac{2a}{Rb} \tag{5.126}$$

It should be borne in mind that Equation (5.125) is only an approximate correlation because the values of a and b vary with temperature and pressure.

EXAMPLE 5.23 The constants a and b for a van der Waals' gas are 1.39×10^{-2} lit^2 atm mol^{-2} and 3.92×10^{-2} lit mol^{-1}, respectively. If the value of the gas constant $R = 0.082$ lit atm deg^{-1} mol^{-1}, calculate the value of the inversion temperature for the gas.

Solution Inversion temperature for the gas

$$T_i = \frac{2a}{Rb} = \frac{2\times1.39}{0.082\times3.92} = \frac{2.78\times1000}{82\times3.92} = 8.64 \text{ K} \quad \blacksquare$$

EXAMPLE 5.24 Prove that

$$dH = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + V\,dP$$

Solution Differentiating $S = f(P,T)$, we get

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT = \left(\frac{\partial S}{\partial P}\right)_T dP + \frac{C_P dT}{T}$$

From Maxwell's relations, we have

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

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Therefore,

$$dS = \frac{C_P dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Now, $H = U + PV$. Thus,

$$dH = dU + P\,dV + V\,dP = dQ + V\,dP$$

or

$$dH = T\,dS + V\,dP$$

$$= T\left[\frac{C_P dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP\right] + V\,dP$$

$$= C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + V\,dP \qquad \blacksquare$$

5.19 PHASE TRANSITION

Let us consider equilibrium between two phases 1 and 2 of a pure substance at constant temperature and pressure. The condition of equilibrium would be given by

$$\Delta G = G_2 - G_1 = 0 \tag{5.127}$$

where the subscripts 1 and 2 represent the two phases. Therefore, $G_2 = G_1$ at equilibrium. Suppose that the temperature changes from T to $T + dT$ and pressure from P to $P + dP$ so that the free energies for the two phases change from G to $G + dG$ in such a way that two phases continue to remain in equilibrium with each other. For such a situation at equilibrium we can write $G_2 + dG_2 = G_1 + dG_1$. Therefore,

$$dG_2 = dG_1 \tag{5.128}$$

Since

$$dG = -S\,dT + V\,dP \tag{5.128a}$$

We have from Equation (5.128a)

$$-S_2\,dT + V_2\,dP = -S_1\,dT + V_1\,dP$$

or

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} \tag{5.129}$$

If we consider 1 g of the pure substance, at equilibrium for the transition process we can write $\Delta S = (\Delta H)/T$, where ΔH is the change in enthalpy for the reversible transformation at temperature T (i.e. latent heat per gram of phase transformation). In view of this, Equation (5.129) would be read as

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T(V_2 - V_1)} \tag{5.130}$$

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where V represents the specific volume. Equation (5.130) is the well-known *Clapeyron's equation*. For equilibrium between solid and liquid phase of a pure substance, Equation (5.130) would be read

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_L - V_S)} \tag{5.131}$$

and in the case of equilibrium between liquid and vapour phase of a pure substance, we have

$$\frac{dP}{dT} = \frac{\Delta H_e}{T(V_{\text{vapour}} - V_L)} \tag{5.132}$$

where the subscripts L, S and 'vapour' represent liquid, solid and vapour phase respectively and ΔH_f and ΔH_e are the latent heats (per gram) of fusion and vaporization respectively. Equation (5.132) can be transformed into a more functional form by incorporating the assumption that $V_{\text{vapour}} \gg V_L$

$$\frac{dP}{dT} = \frac{\Delta H_e}{TV_{\text{vapour}}} \tag{5.133}$$

If the vapour behaves ideally, we can rewrite

$$\frac{dP}{dT} = \frac{\Delta H_e}{RT^2} P \tag{5.134}$$

Assuming ΔH_e remains constant between the limits of integration, Equation (5.134) can be integrated to yield

$$\int_{P_1}^{P_2} \frac{dP}{P} = \Delta H_e \int_{T_1}^{T_2} \frac{dT}{RT^2}$$

or

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_e}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.135}$$

which is the integrated form of Clapeyron's equation for the vapour–liquid equilibrium. To arrive at more precise result we can consider the temperature dependence of ΔH while integrating.

Trouton's rule

Rearranging Equation (5.134), we get

$$\frac{dP}{P} = \frac{\Delta H_e}{RT^2} dT$$

or

$$\int \frac{dP}{P} = \frac{\Delta H_e}{R} \int \frac{dT}{T^2}$$

or

$$\ln P = -\frac{\Delta H_e}{RT} + C$$

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where C is a constant. At normal boiling point (T_b) the vapour pressure $P = 1$ atm. Therefore,

$$\frac{\Delta H_e}{RT_b} = C \quad \text{or} \quad \frac{\Delta H_e}{T_b} = RC = \text{constant}$$

According to Trouton, the value of this constant is 85 JK^{-1} mol^{-1}. Hence,

$$\frac{\Delta H_e}{T_b} = 85 \text{ JK}^{-1}\text{mol}^{-1} = \Delta_{\text{vapour}} S$$

Therefore, entropy of vaporization for all liquids (except hydrogen bonding and other kind of specific bonding is present) at their boiling temperature are same.

EXAMPLE 5.25 In case of fusion or melting, determine the relation between temperature and pressure. What should be nature of boundary line between a liquid and a solid phase in phase diagram.

Solution We know,

$$\frac{dP}{dT} = \frac{\Delta H_f}{T\Delta V}$$

Here $\Delta V = V_L - V_S$. In case of solid or liquid, the molar volume is independent of temperature and much less than the molar volume of a gas. Therefore, in case of fusion or melting, ΔV remains constant. If ΔH also remains constant, then we can write

$$\int_{P_1}^{P_2} dP = \frac{\Delta H}{\Delta V}\int_{T_1}^{T_2} \frac{dT}{T}$$

where ΔH is the enthalpy change for fusion or melting. Thus, we get

$$P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln \frac{T_2}{T_1} \quad \blacksquare$$

EXAMPLE 5.26 The variation of the vapour pressure of ethylene with temperature is given by the equation:

$$\log P = -\frac{834.13}{T} + 1.75 \log T - 8.375 \times 10^{-3} T + 5.3234 \qquad (1)$$

Calculate the enthalpy of vaporization of ethylene at its boiling point, −103.9°C.

Solution We know that

$$\frac{d \ln P}{dT} = \frac{\Delta H_e}{RT^2}$$

Rewriting the given Equation (1) as

$$\frac{1}{2.303} \ln P = -\frac{834.13}{T} + \frac{1.75}{2.303} \ln T - 8.375 \times 10^{-3} T + 5.3234$$

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and differentiating it with respect to temperature (T), we get

$$\frac{d \ln P}{dT} = \frac{2.303 \times 834.13}{T^2} + \frac{1.75}{T} - 2.30 \times 8.375 \times 10^{-3}$$

Substituting $R = 8.314$ JK^{-1} mol^{-1} and $T = -103.9 + 273.15 = 169.25$ K in the above equation, we find that $\Delta H_e = 13.84$ kJ mol^{-1}. ■

EXAMPLE 5.27 The boiling point of benzene at 101.3 kPa is 353.2 K. Find out the boiling point of benzene at 60 kPa. The enthalpy of vaporization of benzene at its boiling point is 31.8 kJ mol^{-1}.

Solution We have

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_e}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\ln \frac{60}{101.3} = -\frac{31.8 \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{T_2} - \frac{1}{353.2 \text{ K}}\right)$$

or

$$0.524 = -3825 \text{ K}\left(\frac{1}{T_2} - \frac{1}{353.2 \text{ K}}\right)$$

or

$$\frac{1}{T_2} = 1.37 \times 10^{-4} \text{ K}^{-1} + \frac{1}{353.2 \text{ K}} = 2.968 \times 10^{-3} \text{ K}^{-1}$$

or

$$T_2 = \frac{1}{2.968 \times 10^{-3} \text{ K}^{-1}} = 336.9 \text{ K} \quad ■$$

EXAMPLE 5.28 The vapour pressure of a pure ethanol at 0°C and at 60°C are respectively 0.016 bar and 0.470 bar. Calculate the normal boiling point of ethanol and its molar enthalpy of vaporization.

Solution We have

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_e}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\ln \frac{0.470}{0.016} = -\frac{\Delta H_e}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}}\left(\frac{1}{333 \text{ K}} - \frac{1}{273 \text{ K}}\right)$$

or

$$3.38 = -\frac{\Delta H_e}{8.314 \text{ J}^{-1} \text{ mol}^{-1}}\left(-6.6 \times 10^{-4}\right)$$

or

$$\Delta H_e = 42.58 \text{ kJ mol}^{-1}$$

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Normal boiling point is the temperature at which vapour pressure is 1 atm = 1.01325 bar. Therefore

$$\ln\frac{1.01325}{0.47} = -\frac{42.58 \text{ kJ mol}^{-1}}{8.314\times10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{T_2} - \frac{1}{333 \text{ K}}\right)$$

or

$$\frac{1}{T_2} - \frac{1}{333\ K} = -1.499\times10^{-4} \text{ K}^{-1}$$

or

$$\frac{1}{T_2} = \left(3.003\times10^{-3} - 1.499\times10^{-4}\right) \text{K}^{-1}$$

Therefore,

Normal boiling point T_2 = 350.5 K = 77.5°C

and

Molar enthalpy of vaporization = 42.58 kJ mol^{-1} ■

EXAMPLE 5.29 The normal boiling point of benzene at 1.01325 bar is 80.2°C. If benzene obeys Trouton's rule, then calculate the vapour pressure of benzene at 25°C.

Solution From Trouton's rule, we have

$$\frac{\Delta H_e}{T_b} = 85 \text{ JK}^{-1} \text{ mol}^{-1}$$

or

$$\Delta H_e = 85\times(80.2+273) \text{kJ K}^{-1} \text{ mol}^{-1} = 30.022 \text{ kJ mol}^{-1}$$

Now,

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H_e}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\ln\frac{1.01325 \text{ bar}}{P_1} = -\frac{30.022 \text{ kJ mol}^{-1}}{8.314\times10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{353.2 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

or

$$\ln\frac{1.01325 \text{ bar}}{P_1} = 1.8938$$

or

$$\frac{1.01325}{P_1} = 6.645$$

Therefore,

$$P_1 = \frac{1.01325 \text{ bar}}{6.645} = 0.152 \text{ bar}$$ ■

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5.20 SYSTEM WITH VARIABLE COMPOSITION

Let us now study the systems consisting of two or more substances (i.e. solutions) of heterogeneous systems containing two or more phases. So far we have confined our attention to closed systems. If the system consists of two or more phases it may be visualized as consisting of several subsystems which are open to each other, the total system, however, continues to be a closed one. In the treatment of such systems the concept of partial molar properties developed by G.N. Lewis is of great value.

Partial molar properties

The state postulate discussed in Chapter 4 is in the context of a closed system whose composition does not vary. The term 'specified system' there meant a closed system having specified amount of specified matter. If composition of the system is also undergoing change, additional variables describing change in the composition should come in. Thus any thermodynamic extensive property say F should be expressed as

$$F = F(T, P, n_1, n_2, \ldots) \tag{5.136}$$

where n_1, n_2 etc., are the number of moles of the respective components 1, 2 etc., of the system. From Equation (5.136), we can write

$$dF = \left(\frac{\partial F}{\partial T}\right)_{P, n_1, n_2, \ldots} dT + \left(\frac{\partial F}{\partial P}\right)_{T, n_1, n_2, \ldots} dP + \left(\frac{\partial F}{\partial n_1}\right)_{T, P, n_2, \ldots} dn_1 + \left(\frac{\partial F}{\partial n_2}\right)_{T, P, n_1, n_3, \ldots} dn_2 + \cdots \tag{5.137}$$

The derivatives

$$\left(\frac{\partial F}{\partial n_i}\right)_{T, P, n_1, n_2, \ldots}$$

in the above equation are called the *partial molar property*. If temperature and pressure are held constant we have from Equation (5.137),

$$(dF)_{T,P} = \bar{F}_1\, dn_1 + \bar{F}_2\, dn_2 + \cdots \tag{5.138}$$

where

$$\bar{F}_1 = \left(\frac{\partial F}{\partial n_1}\right)_{T, P, n_2, n_3, \ldots}; \qquad \bar{F}_2 = \left(\frac{\partial F}{\partial n_2}\right)_{T, P, n_1, n_3, \ldots} \tag{5.139}$$

and so on. For a system of definite composition[4] represented by

4. Fixed composition has been symbolized as N.

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n_1, n_2, ... integrating Equation (5.138), we get

$$F_{T,P,N} = n_1\bar{F}_1 + n_2\bar{F}_2 + \cdots \tag{5.140}$$

Differentiation of Equation (5.140), at constant T and P but at varying n, gives

$$\begin{aligned}(dF)_{T,P} &= \left(n_1 d\bar{F}_1 + \bar{F}_1\, dn_1\right) + \left(n_2 d\bar{F} + \bar{F}_2 dn_2\right) + \cdots \\ &= \left(nd\bar{F}_1 + n_2 d\bar{F}_2 + \cdots\right) + \left(\bar{F}_1 dn_1 + \bar{F}_2 dn_2 + \cdots\right)\end{aligned} \tag{5.141}$$

Comparing Equations. (5.138) and (5.141), it follows that at constant T and P

$$n_1 d\bar{F}_1 + n_2 d\bar{F}_2 + \cdots = 0 \tag{5.142}$$

Equation (5.142) is the well known *Gibbs–Duhem equation* which must obviously be applicable to a system of definite composition. It suggests that the partial molar properties cannot change independently of one another. The increase of one partial molar property should be compensated by some other partial molar property. It is obvious from Equation (5.139) that the partial molar property represents the change of the property with the change in the number of moles of the component when temperature and pressure and the number of moles of other components of the system are held constant.

5.21 CHEMICAL POTENTIAL

Chemical potential was defined by Gibbs as the partial molar Gibbs' free energy, i.e.

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots} = \mu_i \tag{5.143}$$

where μ_i is the chemical potential of the component i. For a multi-component system, writing G as

$$G = G\,(T, P, n_1, n_2 \ldots) \tag{5.144}$$

We can write an equation analogous to Equation (5.137), i.e.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \sum_i \mu_i\, dn_i \tag{5.145}$$

In the particular case, where there is no change in the number of moles of the various components, i.e. dn_1, dn_2, etc., are all zero (closed systems), Equation (5.145) reduces to

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP \tag{5.146}$$

Comparing Equations (5.146) and (5.105) for closed system, we have

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

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Now, with the help of the above equations, Equation (5.145) can be written as

$$dG = -S\,dT + V\,dP + \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_i\,dn_i + \cdots \tag{5.147}$$

which at constant temperature and pressure, reduces to

$$(dG)_{T,P} = \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_i\,dn_i + \cdots \tag{5.148}$$

Hence, Equation (5.148) has the same form as of Equation (5.138). The Gibbs–Duhem equation in this case corresponding to Equation (5.142) can easily be deduced. It would be

$$n_1\,d\mu_1 + n_2\,d\mu_2 + \cdots + n_i d\mu_i + \cdots = 0 \tag{5.149}$$

If the system is at equilibrium under constant temperature and pressure, $(dG)_{T,P}$ will be equal to zero (Equation 5.99). Thus from Equation (5.148), we get

$$\sum \mu_i\,dn_i = 0 \tag{5.150}$$

which represents the condition of equilibrium at constant T and P for the systems of variable composition. For example, equilibrium at constant T and P, between the various phases, open to each other constituting an overall closed system would be governed by Equation (5.150). As we will see, Equation (5.150) is the basis of the well-known Gibbs phase rule.

There can be several alternative definitions of the chemical potential defined by Equation (5.143). For example, chemical potential can be defined in terms of enthalpy H or internal energy U, where

$$H = G + TS$$

or

$$dH = dG + T\,dS + S\,dT \tag{5.151}$$

But we know that

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_i dn_i + \cdots \tag{5.147}$$

From Equations (5.147) and (5.151), we can write

$$dH = T\,dS + V\,dP + \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_i\,dn_i + \cdots \tag{5.152}$$

From Equation (5.152), it follows that

$$\left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_2\ldots} = \mu_1, \quad \left(\frac{\partial H}{\partial n_2}\right)_{S,P,n_1,n_3,\cdots} = \mu_2, \text{ and so on} \tag{5.153}$$

By means of similar arguments we can define chemical potentials in terms of internal energy U and work function A. Thus,

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\cdots} = \left(\frac{\partial H}{\partial n_1}\right)_{S,P,n_2,\cdots} = \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2,\cdots} = \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2,\cdots} \tag{5.154}$$

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5.22 VARIATIONS OF CHEMICAL POTENTIALS WITH TEMPERATURE AND PRESSURE

Chemical potential of the ith component in a multi-component system is

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}, \qquad \text{where } j \neq i$$

Differentiating the above equation with respect to T at constant pressure and composition, we get

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right]_{P,n_i} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial T}\right)_{P,n_i}\right]_{T,P,n_j} \tag{5.155}$$

Since

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S$$

From Equation (5.155), we have

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j} = -\bar{S}_i \tag{5.156}$$

where $\bar{S}_i$ is the partial molar entropy of the component i. Also, from the definition $G = H - TS$, it follows that

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}$$

or

$$\mu_i = \bar{H}_i - T\bar{S}_i \tag{5.157}$$

where $\bar{H}_i$ is the partial molar enthalpy of the component i. Using Equation (5.156) in Equation (5.157), we obtain

$$\mu_i - T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = \bar{H}_i \tag{5.158}$$

or

$$\left[\frac{\partial(\mu_i/T)}{\partial T}\right]_{P,N} = -\frac{\bar{H}_i}{T^2}$$

which is nothing but the *Gibbs Helmholtz equation* written in terms of partial molar quantities.

Variation with pressure

Writing the chemical potential as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}, \qquad \text{where } j \neq i$$

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and differentiating μ_i with respect to pressure, holding temperature and composition constant, we get

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right]_{T,n_i} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial P}\right)_{T,n_i}\right]_{T,P,n_j} \tag{5.159}$$

In writing Equations (5.155) and (5.159), the fact that dG is an exact differential has been utilized. Since $\left(\partial G/\partial P\right)_{T,n_i} = V$, we have from Equation (5.159)

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} = \bar{V}_i \tag{5.160}$$

where $\bar{V}_i$ is the partial molar volume of the component i.

For a system of ideal gases, Equation (5.160) can be further simplified. Suppose a system consists of n_1, n_2, ... moles of ideal gases 1, 2, ... For such a case, we can write

$$V = \left(n_1 + n_2 + \cdots\right)\frac{RT}{P} \tag{5.161}$$

and for $j \neq i$, we have

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} = \bar{V}_i = \frac{RT}{P} \tag{5.162}$$

Now, using Equation (5.162) in (5.160), we can write

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{RT}{P} \tag{5.163a}$$

or

$$\int_{\mu_i^\circ}^{\mu_i} d\mu_i = RT\int_{P_0}^{P}\frac{dP}{P} \tag{5.163b}$$

or

$$\mu_i = \mu_i^\circ + RT\ln\frac{P}{P_0} \tag{5.163c}$$

If P_i = 1 atm, μ_i° = standard chemical potential of the gas and is a function of temperature only. Therefore, we can write from Equation (5.163c),

$$\mu_i\left(T,P\right) = \mu_i^\circ\left(T\right) + RT\ln P \tag{5.164}$$

Thus at a given temperature, pressure is the measure of the chemical potential of a gas. The chemical potential can also be written in terms of partial pressures

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of gas in mixture of gases. We know that in mixture of gases the partial pressure p_i of the gas i is related to the total pressure by the equation:

$$p_i = \frac{n_i}{n} P = x_i P \tag{5.165}$$

where $n = n_1 + n_2 + \cdots$ and x_i is the mole fraction. Using Equation (5.165) in Equation (5.163a) and imposing the condition that x_i = constant, we have

$$d\mu_i = RTd \ln p_i \tag{5.166}$$

which on integration yields the relationship

$$\mu_i = \mu_i^* + RT \ln p_i \tag{5.167}$$

where μ_i^* is the constant of integration, whose value depends on the nature of the gas and also on temperature. The partial pressure p_i of an ideal gas is related to its concentration C in the mixture by equation:

$$p_i = C_i RT \tag{5.168}$$

Introducing p_i in Equation (5.167), we get

$$\mu_i = \mu_C^* + RT \ln C_i \tag{5.169}$$

where $\mu_C^* = \mu^* + RT \ln (RT)$. Thus μ_C^* for the given gas depends on the temperature. If Equation (5.165) is introduced in Equation (5.167) we can write the chemical potential in terms of mole fraction, i.e.

$$\mu_i = \mu_{x_i}^* + RT \ln x_i \tag{5.170}$$

where $\mu_{x_i}^* = \mu_i^* + RT \ln P$. Thus $\mu_{x_i}^*$ depends on both temperature and total pressure P.

Equations for chemical potential listed above assume the ideal behaviour. For non-ideal situations (real gases and solutions), a correction factor γ_i known as 'activity coefficient' is introduced. The value of γ_i normally ranges between 0 and 1. For substances behaving ideally $\gamma_i = 1$.[5] With this correction, equations for chemical potentials would be modified, e.g. Equation (5.167) would read as

$$\mu_i = \mu_i^* + RT \ln \left(\gamma_i P_i\right) \tag{5.171}$$

For dilute solutions, however, where $\gamma \rightarrow 1$, equations such as Equations (5.167) and (5.170) are good approximations and can be safely used.

5.23 WRITING FREE ENERGY CHANGE FOR A PROCESS

The free energy change for any process can be written as the difference between the free energies in the final state and in the initial state. Suppose in a particular process n_1, n_2, ... moles of the components 1, 2, ... are transformed into n_1',

5. This correction factor and the methods for its measurement are explained in Chapter 6.

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n'_2 ... moles of the components 1', 2', ..., the free energy change of the process would be given by

$$\Delta G = \left(n'_1 \mu'_1 + n'_2 \mu'_2 + \cdots\right) - \left(n_1 \mu_1 + n_2 \mu_2 + \cdots\right) \tag{5.172}$$

Now, we are in a position to take up some of the representative applications of the chemical potential concept.

5.24 APPLICATIONS OF CHEMICAL POTENTIAL

5.24.1 Phase Rule

Let us first take up the derivation of the famous Gibbs' phase rule. Consider a closed system consisting of 1, 2, ..., c components and a, b, c, ..., p phase such that each of the c components is existing in each of the p phases. The situation is shown as in Figure 5.10.

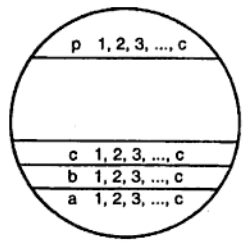

Figure 5.10 Schematic depiction of a system consisting of p phases; each phase having c components.

The total system is a closed system and consists of subsystems which are open to each other. If the total system is at constant temperature and pressure and is at equilibrium, using Equation (5.150), we can write

$$\begin{aligned}
&\mu_1(a)dn_1(a) + \mu_1(b)dn_1(b) + \cdots + \mu_1(p)dn_1(p) \\
&\quad + \mu_2(a)dn_1(a) + \mu_2(b)dn_2(b) + \cdots + \mu_2(p)dn_2(p) \\
&\quad + \cdots + \mu_c(a)dn_c(a) + \mu_c(b)dn_c(b) + \cdots + \mu_c(p)dn_c(p) = 0
\end{aligned} \tag{5.173}$$

where $\mu_1(a)$, $\mu_2(a)$, ..., $\mu_c(a)$, etc., represent the chemical potentials of the component 1, 2, ..., c etc., in the various phases represented by the subscripts a, b, ..., p in the brackets and n represents the number of moles of the component in various phases representing the subscripts. Since the total system is a closed system, we can write using the law of mass conservation that

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$$\left.\begin{aligned} dn_1(a)+dn_1(b)+\cdots+dn_1(p)&=0\\ dn_2(a)+dn_2(b)+\cdots+dn_2(p)&=0\\ \vdots\qquad\quad\vdots&\qquad\quad\vdots\\ dn_c(a)+dn_c(b)+\cdots+dn_c(p)&=0 \end{aligned}\right\} \tag{5.174}$$

If Equations (5.174) and (5.173) are to be obeyed simultaneously it is essential that

$$\left.\begin{aligned} \mu_1(a)=\mu_1(b)=\cdots&=\mu_1(p)\\ \mu_2(a)=\mu_2(b)=\cdots&=\mu_2(p)\\ \vdots\qquad\quad\vdots&\qquad\quad\vdots\\ \mu_c(a)=\mu_c(b)=\cdots&=\mu_c(p) \end{aligned}\right\} \tag{5.175}$$

Thus it is seen that when a closed system consisting of a number of phases containing a number of components is in equilibrium at constant temperature and pressure the chemical potential of each component is the same in all the phases. In fact the set of Equations (5.175) represents conditions of equilibrium between the phases. If the chemical potentials of any component between two phases are unequal the flowing tendency of the matter will be from the phase with higher chemical potential of the component to the phase with the lower chemical potential till the chemical potentials of the component in the two phases equalize, i.e. equilibrium is reached.

The result contained in Equation (5.175) can be utilized to deduce the Gibbs' phase rule which is the relationship between the number of components, number of phases and the number of degree of freedom. By the term 'number of degrees of freedom' we mean the number of variables which must be arbitrarily fixed to define a system. In order to define the closed system depicted in Figure 5.10, one must, in addition to temperature and pressure, define the number of concentration terms. So, the main problem is to know the number of concentration terms. The number of concentration terms, for any phase, should be equal to $(c - 1)$. This is because if the concentration of all but one component is specified the concentration of the last component is automatically fixed. Since there are p such phases the total number of concentration terms for the total system would be $p(c - 1)$. In addition to $p(c - 1)$ concentration terms, temperature and pressure are also to be specified. Thus, if surface or electrical effects are absent, the total number of variables = $p(c - 1) + 2$. The fact that at equilibrium at a given temperature and pressure, the set of $c(p - 1)$ independent equations represented by Equation (5.175) are obeyed, implies that $c(p - 1)$ variables are automatically fixed. Hence, the number of variables which remain to be fixed = $[p(c - 1) + 2] - [c(p - 1)] = c - p + 2$. This number is called the *number of degrees of freedom* and is represented by F. Hence, we have

$$F = c - p + 2 \tag{5.176}$$

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Equation (5.176) is the well-known *Gibbs' phase rule*. If $c = 1$ and $p = 3$, F works out to be equal to zero. The equilibrium between liquid water, water vapour and solid water (ice)—the triple point represents this situation.

EXAMPLE 5.30 What is the number of degrees of freedom when only the liquid CO_2 is in equilibrium with the gaseous CO_2?

Solution We know $F = c - p + 2$. Here

$$\text{Number of components } c = 1 \quad (\text{only } CO_2)$$

and

$$\text{Number of phases } p = 2(\text{liquid} + \text{gas})$$

Therefore

$$\text{degrees of freedom } F = 1 - 2 + 2 = 1$$

Degrees of freedom '1' means that either pressure or temperature can be varied independently, i.e. when temperature is fixed, pressure is automatically fixed. ■

EXAMPLE 5.31 Find out the values of degrees of freedom for a one-component system when only one phase is present.

Solution We have

$$F = c - p + 2$$

Here $c = 1$, $p = 1$. Therefore, $F = 1 - 1 + 2 = 2$, i.e. both pressure and temperature can be varied independently. ■

5.24.2 Lowering of Vapour Pressure/Roult's Law

When a non-volatile solute is added to a volatile solvent the vapour pressure of the solvent (over the solution) is lowered in comparison to the vapour pressure of the pure solvent (over the pure solvent). If P^* and P are respectively the vapour pressures of the pure solvent and solvent (over the solution), we have the relationship:

$$P_i = P_i^* x_i \tag{5.177}$$

where x_i is the mole fraction of the solvent in the solution. Here, the temperature

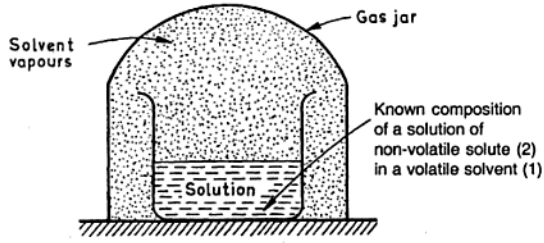

Figure 5.11 Solution of non-volatile solute in a volatile solvent kept under a jar at constant temperature and pressure.

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is held constant. The relationship (5.177) is the well-known *Roult's law*. We shall now deduce Equation (5.177) using the concept of chemical potential.

Let us consider the system depicted in Figure 5.11.

A beaker containing the solution of known composition of a non-volatile solute in a volatile solvent is covered by a glass jar. The temperature is kept constant. Figure 5.11 essentially represents the situation of equilibrium between two phases. When equilibrium is attained we can write

$$\mu_1^l = \mu_1^v$$

or

$$d\mu_1^l = d\mu_1^v \tag{5.178}$$

where the superscripts l and v represent the liquid and the vapour phase, respectively. The chemical potential of the solvent (1) in the liquid phase depends on the temperature T, pressure P and the composition of solvent in solution (x_1). That is,

$$\mu_1^l = f(T, P, x_1)$$

or

$$d\mu_1^l = \left(\frac{\partial \mu_1^l}{\partial T}\right)_{P,x_1} dT + \left(\frac{\partial \mu_1^l}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{T,P} dx_1 \tag{5.179}$$

Since temperature is held constant

$$dT = 0 \quad \text{and} \quad \left(\frac{\partial \mu_1^l}{\partial P}\right)_{T,x_1} = \overline{V}_1^L$$

the partial molar volume of solvent in the liquid phase and

$$\left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{T,P} = \frac{RT}{x_1}$$

Equation (5.179) would read as

$$d\mu_1^l = \overline{V}_1^l \, dP + RT \frac{dx_1}{x_1} \tag{5.180}$$

In writing Equation (5.180) from (5.179) the definition $\mu_i = \mu_i^* + RT \ln x_i$ has been utilized. Since the solute is non-volatile it would not be present in the vapour phase. Therefore the chemical potential of the solvent in the vapour phase would be determined only by temperature and pressure, i.e.

$$\mu_1^v = f(T, P)$$

or

$$d\mu_1^v = \left(\frac{\partial \mu_1^v}{\partial T}\right)_P dT + \left(\frac{\partial \mu_1^v}{\partial P}\right)_T dP \tag{5.181}$$

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Since

$$dT = 0 \quad \text{and} \quad \left(\frac{\partial \mu_1^v}{\partial P}\right) = \bar{V}_1^v$$

the partial molar volume of the solvent in the vapour phase, Equation (5.181), would be read as

$$d\mu_1^v = \bar{V}_1^v dP \tag{5.182}$$

In view of Equation (5.178), we can write from Equations (5.180) and (5.182) that

$$\bar{V}_1^v \, dP = \bar{V}_1^l \, dP + RT \frac{dx_1}{x_1}$$

or

$$\left(\bar{V}_1^v - \bar{V}_1^l\right) dP = RT \frac{dx_1}{x_1} \tag{5.183}$$

Since $\bar{V}_1^v \gg \bar{V}_1^l$ we can write from Equation (5.183)

$$\bar{V}_1^v dP = RT \frac{dx_1}{x_1} \tag{5.184}$$

If the vapour behaves ideally we can further write from Equation (5.184) that

$$d \ln P = d \ln x_1 \tag{5.185}$$

Integrating Equation (5.185) between the limits $x = 1$, $P_1 = P_1^*$ and $x = x_1$, $P = P_1$, we get

$$\int_{P_1^*}^{P_1} d \ln P = \int_1^{x_1} d \ln x_1$$

or

$$P_1 = P_1^* x_1 \tag{5.177}$$

which is the well-known Roult's law equation.

To derive equation for the relative lowering of vapour pressure let us rewrite Equation (5.177) in the form

$$P_1 = P_1^* \left(1 - x_2\right)$$

or

$$\frac{P_1^* - P_1}{P_1^*} = x_2 \tag{5.186}$$

which is the familiar equation in solution chemistry and state that the relative lowering of vapour pressure $(P_1^* - P_1)/P_1^*$ is equal to the mole fraction of the solute in solution.

EXAMPLE 5.32 The vapour pressure of pure water at 20°C is 1.75×10^{-5} torr. At what mole fraction of sucrose the vapour pressure of water will be lowered by 1.1×10^{-5} torr?

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Solution As

$$P_1 = P_1^* x_1 = P_1^* (1 - x_2)$$

Then

$$P_1 = P_1^* - P_1^* x_2$$

Hence

$$x_2 = \frac{P_1^* - P_1}{P_1^*} = \frac{1.1 \times 10^{-7}}{1.75 \times 10^{-5}} = 6.286 \times 10^{-3} \quad \blacksquare$$

EXAMPLE 5.33 What would be the partial vapour pressure of benzene over the solution which is prepared by dissolving 5-mol naphthalene in 20-mol benzene? Given the vapour pressure of pure benzene is 94.6 torr at 25°C.

Solution We have

$$P_1 = P_1^* x_1 = P_1^* \frac{n_1}{n_1 + n_2}$$

Then

$$P_1 = 94.6 \times \frac{20}{20+5} = 75.68 \text{ torr} \quad \blacksquare$$

EXAMPLE 5.34 What would be the reduction in chemical potential of toluene at 25°C when a solute is added at a mole fraction of 0.28?

Solution As

$$\mu_A = \mu_A^* + RT \ln x_A$$

where μ_A is chemical potential of solvent in solution, μ_A^* is chemical potential of pure solvent and x_A is the mole fraction of the solvent in the solution. Therefore,

$\mu_A^* - \mu_A = -RT \ln x_A = -8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \ln(1 - 0.28) = -813.9 \text{ J mol}^{-1}$

Thus, reduction in chemical potential is 813.9 J mol^{-1}. $\blacksquare$

5.24.3 Elevation of Boiling Point

When a non-volatile solute is added to a volatile solvent the boiling point of the pure solvent is elevated and this elevation in boiling point is related to the composition of the solution. This relationship can be easily deduced using the concept of chemical potential.

Let us consider the equilibrium between the liquid and the vapour phase when the solution is boiling. Equation (5.178) can be written for this situation as well. Since the solute is non-volatile chemical potential of solvent in the liquid phase (μ_1^l) and the chemical potential of the solvent in the vapour phase (μ_1^v), would be given by Equations (5.179) and (5.181), respectively. Also, since

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$$\left(\frac{\partial \mu_1^l}{\partial T}\right)_{P,x_1} = -\bar{S}_1^l \quad \text{and} \quad \left(\frac{\partial \mu_1^v}{\partial T}\right)_{P,x_1} = -\bar{S}_1^v \tag{5.187}$$

where $\bar{S}_1^l$ and $\bar{S}_1^v$ are the partial molar entropies of the solvent in the liquid and in the vapour phase respectively. Equations for $d\mu_1^l$ and $d\mu_1^v$ using Equations (5.179) and (5.181) can be rewritten as

$$d\mu_1^l = -\bar{S}_1^l\, dT + \bar{V}_1^l\, dP + RT\frac{dx_1}{x_1} \tag{5.188}$$

and

$$d\mu_1^v = -\bar{S}_1^v\, dT + \bar{V}_1^v dP \tag{5.189}$$

Equations (5.188) and (5.189) in view of Equation (5.178) yield the relationship

$$\left(\bar{S}_1^v - \bar{S}_1^l\right)dT + \left(\bar{V}_1^l - \bar{V}_1^v\right)dP + RT\frac{dx_1}{x_1} = 0 \tag{5.190}$$

Since usually boiling is carried out at constant pressure, $dP = 0$, we have from Equation (5.190)

$$\Delta\bar{S}\, dT = \left(\bar{S}_1^v - \bar{S}_1^l\right) dT = -RT\frac{dx_1}{x_1} \tag{5.191}$$

Here $\Delta\bar{S} = \Delta H_{\text{vapour}}/T$, we get from Equation (5.191)

$$d \ln x_1 = -\frac{\Delta H_{\text{vapour}}}{RT^2} dT \tag{5.192}$$

where ΔH_{vapour} is the molar heat of vaporization of the solvent. Integrating Equation (5.192) under the limits $x_1 = 1$, $T = T_b$, the boiling point, we get

$$\int_1^{x_1} d \ln x_1 = -\frac{\Delta H_{\text{vapour}}}{R}\int_{T_b}^{T}\frac{dT}{T^2} \tag{5.193}$$

Assuming that ΔH_{vapour} remains more or less constant in the temperature range we have in Equation (5.193)

$$\ln x_1 = \frac{\Delta H_{\text{vapour}}}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right)$$

or

$$\ln(1 - x_2) = \frac{-\Delta H_{\text{vapour}}}{R}\frac{\Delta T_b}{TT_b} \tag{5.194}$$

where $\Delta T_b = T - T_b$. If T and T_b are close to each other so that ΔH may be taken to be constant and $TT_b \approx T_b^2$ and the solution is a dilute solution, i.e. $x_2 << 1$, Equation (5.194) can be written as

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$$\ln(1-x_2) = -x_2 = -\frac{\Delta H_{\text{vapour}}}{RT_b^2}\Delta T_b$$

or

$$x_2 = \frac{\Delta H_{\text{vapour}}}{RT_b^2}\Delta T_b \tag{5.195}$$

which is a well-known relationship between the elevation of boiling point on the composition of the solution. Now in dilute solution

$$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$$

Therefore, from Equation (5.195), we can write

$$\Delta T_b = \frac{RT_b^2 x_2}{\Delta H_{\text{vapour}}} = \frac{RT_b^2}{\Delta H_{\text{vapour}}}\frac{W_2}{M_2}\frac{M_1}{W_1}$$

Here W and M represent weight and molar mass, respectively. 1 and 2 represent solvent and solute, respectively. Then

$$\Delta T_b = \frac{RT_b^2}{\Delta H_{\text{vapour}}/M_1}\frac{W_2}{M_2W_1} = \frac{RT_b^2}{\Delta H'_{\text{vapour}}}\frac{W_2}{M_2W_1}$$

where $\Delta H'_{\text{vapour}}$ is the enthalpy of vaporization per gram. Now,

$$\Delta T_b = \frac{RT_b^2}{\Delta H'_{\text{vapour}}}\frac{W_2}{M_2W_1} = \frac{RT_b^2}{\Delta H'_{\text{vapour}}}m$$

where m is the molality of the solution. Therefore,

$$\frac{RT_b^2}{\Delta H'_{\text{vapour}}} = K_b = \text{ebullioscopic constant of the solvent}$$

Hence $\Delta T_b = K_b m$.

Similar relationship can be deduced between the depression in freezing point and the composition of the solution. This deduction is left to the student as an exercise. Here $\Delta T_f = K_f m$, where ΔT_f is depression in freezing point, K_f is cryoscopic constant of the solvent and m is molality of the solution.

EXAMPLE 5.35 Estimate the boiling point of a solution which is made by dissolving 155 g of glucose (mol wt. = 180) in 1000 g of water. Given ebullioscopic constant, K_b of water is 0.51 K kg mol^{-1}.

Solution Here

$$155 \text{ g of glucose} = \frac{155}{180} = 0.861 \text{ mol}$$

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Then

$$m = \frac{0.861 \text{ mol}}{1 \text{ kg}} = 0.861 \text{ mol kg}^{-1}$$

We also have

$$\Delta T_b = T_f - T_i = 0.51 \text{ K kg mol}^{-1} \times 0.861 \text{ mol kg}^{-1} = 0.44 \text{ K}$$

Therefore,

$$T_f = (373 + 0.44) \text{ K} = 373.44 \text{ K or } 100.44°\text{C} \quad \blacksquare$$

EXAMPLE 5.36 The freezing point of pure benzene is 5.44 K. When 2.12 g of a solute is dissolved in 125 g of benzene the freezing point of the solution is 4.63 K. Calculate the molar mass of the solute. Given cryoscopic constant of pure benzene = 5.12 K kg mol^{-1}.

Solution We have $\Delta T_f = K_f m$, where molality m is the number of moles of solute present in 1 kg of solvent. Therefore,

$$m = \frac{2.12 \times 1000}{M_2 \times 125} \text{ mol kg}^{-1}$$

where M_2 is the molar mass of solute. Hence

$$(5.44 - 4.63)\text{K} = 5.1 \text{ K kg mol}^{-1} \times \frac{2.12 \times 1000}{M_2 \times 125} \text{ mol kg}^{-1}$$

or

$$M_2 = \frac{86.496}{0.81} = 106.8 \quad \blacksquare$$

5.24.4 Mixing

The thermodynamic functions of mixing can be conveniently deduced using the concept of chemical potentials.

Free energy (ΔG_{mixing})

Let us consider a two-compartment vessel initially containing n_1 and n_2 moles of two different gases in two different compartments. The partitions is then removed and the two gases are allowed to mix. The situation is depicted in Figure 5.12.

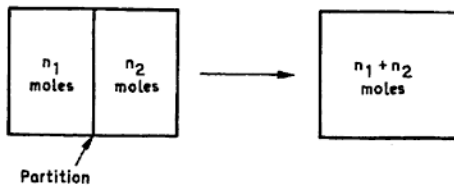

Figure 5.12 Mixing of two gases at the same temperature and pressure.

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In the initial state, we have

$$G \text{ (initial)} = n_1\mu_1^* + n_2\mu_2^* = \sum n_i\mu_i^* \tag{5.196}$$

where μ_i^* is the chemical potential of the pure gas. In the final state, we have

$$G \text{ (final)} = n_1\mu_1 + n_2\mu_2 = \sum n_i\mu_i \tag{5.197}$$

where μ_i is the chemical potential of the gas i in the mixture. Therefore,

$$\Delta G_{\text{mixing}} = \sum n_i\mu_i - \sum n_i\mu_i^* \tag{5.198}$$

Since $\mu_i = \mu_i^* + RT \ln x_i$, we have from Equation (5.198)

$$\Delta G_{\text{mixing}} = RT \sum n_i \ln x_i = nRT \sum \frac{n_i}{n} \ln x_i \tag{5.199}$$

where $\Sigma n_i = n$. Recognizing that $n_i/n = x_i$, we can rewrite (5.199) in the form

$$\Delta G_{\text{mixing}} = nRT \sum x_i \ln x_i \tag{5.200}$$

Entropy of mixing (ΔS_{mixing})

Since $\left(\partial G/\partial T\right)_P = S$, we can write from Equation (5.200) that

$$\Delta S_{\text{mixing}} = -\left[\frac{\partial\left(\Delta G_{\text{mixing}}\right)}{\partial T}\right]_{P,x_i} = -nR \sum x_i \ln x_i \tag{5.201}$$

ΔS_{mixing} in view of Maxwell Demon Bottle (MDB)

Expression for ΔS_{mixing} can be conveniently deduced using MDB discussed earlier in this chapter. The treatment based on MDB will be discussed here because of its didactic value; it is likely to clarify the concepts.

Mixing has a meaning only when the species being mixed are different from each other. For example, if we mix two samples of oxygen we will get only the extensive effects and no effects due to mixing. However, if a sample of oxygen is mixed with a sample of nitrogen, effects due to mixing would become visible.

Let us see what it would mean in terms of MDB. When two MDBs (say 1 and 2), each having two black balls and one white balls, the massless spacer are joined to form the total system, 1 + 2, extensive effects in entropy are observed:

$$S_{1+2} = S_1 + S_2 \tag{5.51}$$

$$\omega_{1+2} = \omega_1 \times \omega_2 \tag{5.53}$$

This is well illustrated in Figures 5.7a and 5.7b. But if one of two MDBs (say 1) has two black balls and one white ball and the other MDB (say 2), has two red balls and one white ball, the situation would be different the number of quantum

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states in the total system (1 + 2) will be more than those given by Equation (5.53), i.e. $\omega_{1+2} > \omega_1 \times \omega_2$. The additional quantum states will be due to the number of

$$\frac{(2+2)!}{2!\,2!} = 6 \text{ ways}$$

the two red balls and two black balls can be permuted in each of these double bottle states. Therefore

$$\omega_{1+2} = \omega_1 \times \omega_2 \times \frac{(2+2)!}{2!\,2!} = 3 \times 3 \times 6 = 54$$

This is well illustrated in Figure 5.13.

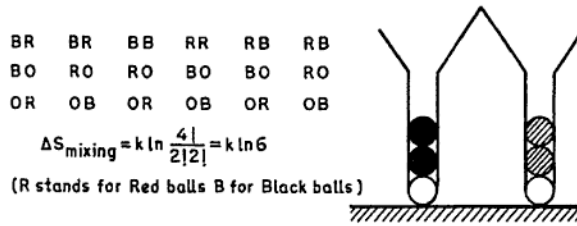

Figure 5.13 Entropy change of mixing as viewed in terms of MDB.

Generalizing this result, we can write

$$\omega_{R+B} = \omega_R \times \omega_B \times \frac{(n_R + n_B)!}{n_B!\,n_R!} \tag{5.202}$$

where the subscripts R, B and $(R + B)$ represent that the quantities are for the MDB with red balls, MDB with black balls and the total MDB obtained by joining the MDB with red and the MDB with black balls, and n_R and n_B, respectively represent the number of red balls and the number of black balls. From Equation (5.202), it follows that

$$\ln \omega_{R+B} = \ln \omega_R + \ln \omega_B + \ln \frac{(n_R + n_B)!}{n_R!\,n_B!}$$

or

$$S_{R+B} = S_R + S_B + k \ln \frac{(n_R + n_B)!}{n_R!\,n_B!} \tag{5.203}$$

The last term on the right-hand side of Equation (5.203) is the contribution due to mixing effect. That is

$$\Delta S_{\text{mix}} = k \ln \frac{(n_R + n_B)!}{n_R!\,n_B!} \tag{5.204}$$

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Making use of Stirling's approximation $\ln n! = n (\ln n) - n$ and recognizing that $n_R + n_B = n$, the total number of balls, Equation (5.204) can be transformed into

$$\Delta S_{\text{mixing}} = -kn\left(\frac{n_R}{n}\ln\frac{n_R}{n} + \frac{n_B}{n}\ln\frac{n_B}{n}\right) \tag{5.205}$$

If R and B are made synonyms with the two chemical species that are mixed and n their number of moles and recognizing that Boltzmann constant k is the ratio of gas constant R to Avagadro number N, Equation (5.205) can be generalized to read as Equation (5.201).

Enthalpy of mixing (ΔH_{mixing})

We know that $\Delta G = \Delta H - T\Delta S$. Therefore,

$$\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}} \tag{5.206}$$

From Equations (5.201), (5.200) and (5.206), it is clear that

$$\Delta H_{\text{mixing}} = 0 \tag{5.207}$$

That is, the enthalpy of mixing of ideal gases is always zero.

Volume of mixing (ΔV_{mixing})

Since $\left(\partial G/\partial P\right)_T = V$, we can write from Equation (5.200) that

$$\Delta V_{\text{mixing}} = \left[\frac{\partial}{\partial P}(\Delta G_{\text{mixing}})\right]_{T,x_i} = 0 \tag{5.208}$$

which means that there is no volume change when ideal gases are mixed.

EXAMPLE 5.37 Calculate the composition at which the molar free energy of mixing of a binary mixture at constant temperature and pressure would be minimum. Assume that the mixture and its components behave ideally.

Solution We know that

$$\Delta G_{\text{mixing}} = RT\left(x_1 \ln x_1 + x_2 \ln x_2\right) = RT\left[x_1 \ln x_1 + \left(1 - x_1\right) \ln \left(1 - x_1\right)\right]$$

ΔG_{mixing} would be minimum when

$$\left[\frac{\partial\left(\Delta G_{\text{mixing}}\right)}{\partial x_1}\right]_{T,P} = 0$$

Therefore,

$$RT\left[\ln x_1 + 1 + \frac{1 - x_1}{1 - x_1}(-1) + (-1) \ln \left(1 - x_1\right)\right] = 0$$

or

$$RT\left[\ln x_1 - \ln\left(1 - x_1\right)\right] = 0$$

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or

$$\ln \frac{x_1}{1-x_1} = 0$$

Thus

$$x_1 = \frac{1}{2} = x_2 \qquad \blacksquare$$

5.24.5 Chemically Reacting Systems

Let us consider a closed system in which the perfectly general reaction represented by the equation

$$aA + bB + \cdots \rightleftharpoons lL + mM + \cdots$$

where lower-case letters represent the stoichiometric coefficients and upper-case letters represent reactants and the products, is allowed to reach state of equilibrium at a given temperature and external (total) pressure. The free energy change of the reaction would be given by

$$\Delta G = \left(l\mu_L + m\mu_M + \cdots\right) - \left(a\mu_A + b\mu_B + \cdots\right) \tag{5.209}$$

Writing

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{5.210}$$

where μ_i° is the chemical potential of the given substance in the chosen standard state of units activity and a_i is the activity of the given substance, we can transform Equation (5.210) into

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_L^l a_M^m \cdots}{a_A^a a_B^b \cdots} \tag{5.211}$$

where

$$\Delta G^\circ = \left(l\mu_L^\circ + m\mu_M^\circ + \cdots\right) - \left(a\mu_A^\circ + b\mu_B^\circ + \cdots\right) \tag{5.212}$$

Let us keep in mind that activity in Equations (5.210) and (5.211) is the product of concentration c_i and the activity coefficient γ_i. At equilibrium, since $(\Delta G)_{T,P} = 0$ it follows from Equation (5.211) that

$$\Delta G^\circ = -RT \ln K = -2.303\, RT \log K \tag{5.213}$$

From Equation (5.213) one discovers the advantage of writing equilibrium constants on the Sorensen's p-scale (p values, p stands for $-\log_{10}$). By knowing the p values one can have an estimate of the ΔG values which is very important for any rate process.

The values of ΔG are helpful in having an idea about the spontaneity of any transformation including chemical reactions. In order to discuss this let us once again look at the conditions of equilibrium [Equations (5.86), (5.87), (5.94) and (5.99)]. Although, it might look like a repeat of what we have done earlier but it is worth using it here. We know that for any transformation

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$$dS \geq \frac{dQ}{T} \tag{5.214}$$

where dS refers to the system alone and not to the net entropy of the system and environment. The equality holds for reversible process and the inequality for the irreversible (spontaneous) ones. The reversible processes should be seen as succession of equilibrium states. Combining with first law we can write from Equation (5.214) that

$$dS \geq \frac{dU + w}{T} \tag{5.215}$$

If U is held constant $dU = 0$ and the $P\,dV$ work is the only work permitted, then at constant U and V it follows from the relationship (5.215) that

$$(dS)_{u,V} \geq 0 \tag{5.216}$$

The obvious conclusion from the relationship (5.216) is that when U and V are held constants the entropy of the system increases in spontaneous (irreversible) processes but remains unaltered when a state of equilibrium is reached. In other words, the entropy of a system at equilibrium at constant energy and volume is maximum.

Similarly combining Equation (5.104) with (5.215), we get

$$dA \leq -W - S\,dT \tag{5.217}$$

The inequality sign holds for spontaneous (irreversible) process. If temperature is held constant ($dT = 0$) and $P\,dV$ work is the only work permitted, the relationship (5.217) at constant T and V would read as

$$(dA)_{T,V} < 0 \tag{5.218}$$

which implies that at constant temperature and volume, when equilibrium is reached, the work function attains a minimum. Under the same conditions, a spontaneous process is accompanied by a decrease in the work function.

When $P\,dV$ work is the only permitted work the relationship (5.215) reads as

$$dS \geq \frac{dU + P\,dV}{T} \tag{5.219}$$

which when combined with Equation (5.105) yields

$$dG \leq V\,dP - S\,dT \tag{5.220}$$

Hence at constant temperature and pressure

$$(dG)_{T,P} \leq 0 \tag{5.221}$$

which means that free energy at constant T and P decreases in a spontaneous process and attains minimum at equilibrium.

It is this result, that a spontaneous process is accompanied by a decrease in free energy is most significant in the present context. Thus, for any transformation (including chemical reactions) at constant temperature and pressure if ΔG is negative the process is spontaneous, otherwise not. Similar conclusion can be

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drawn from the constant temperature and volume. In the context of chemical reactions another term called affinity of the chemical reaction (A_f) is defined as

$$A_f = -\Delta G \tag{5.222}$$

If affinity is positive the chemical reaction is spontaneous, otherwise not. Even without recourse to thermodynamics we can arrive at this conclusion. For any transport process the spontaneous process is always from a higher potential to a lower potential. Thus the free energy of the products should be lower than the free energy of reactants—free energy is a potential.

Let us now deduce an expression for the variation of equilibrium constant with temperature. Consider the following general but simple reaction

$$aA + bB \rightleftharpoons lL + mM$$

For this reaction we can write

$$\Delta G^\circ = \left(l\mu_L^\circ + m\mu_M^\circ\right) - \left(a\mu_A^\circ + b\mu_B^\circ\right) = -RT \ln K \tag{5.223}$$

Differentiating Equation (5.223) with respect to temperature at constant pressure, we have

$$\frac{d \ln K}{dT} = -\frac{1}{R}\left\{l\left[\frac{\partial}{\partial T}\left(\frac{\mu_L^\circ}{T}\right)\right]_P + \left[\frac{\partial}{\partial T}\left(\frac{\mu_M^\circ}{T}\right)\right]_P\right\}$$

$$-\left\{a\left[\frac{\partial}{\partial T}\left(\frac{\mu_A^\circ}{T}\right)\right]_P + b\left[\frac{\partial}{\partial T}\left(\frac{\mu_B^\circ}{T}\right)\right]_P\right\} \tag{5.224}$$

From Gibbs–Helmholtz equation, we know that

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_i^\circ}{T}\right)\right]_P = -\frac{H_i^\circ}{T^2} \tag{5.225}$$

Therefore, Equation (5.224) can be transformed into

$$\frac{d \ln K}{dT} = \frac{1}{RT^2}\left[\left(lH_L^\circ + mH_M^\circ\right) - \left(aH_A^\circ + bH_B^\circ\right)\right] \tag{5.226}$$

In generalized terms, we can write

$$\frac{d \ln K}{dT} = \frac{1}{RT^2}\left[\Sigma H_{\text{products}}^\circ - \Sigma H_{\text{reactants}}^\circ\right] \tag{5.227}$$

or

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{5.228}$$

where ΔH° is the standard enthalpy of the reaction. The following conclusions automatically follow from Equation (5.228).

(a) For exothermic reaction ΔH° is negative and therefore increase in temperature should be accompanied by the decrease in the value K, i.e.

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lesser quantity of product should be formed. Thus for exothermic reactions product formation is favoured at low temperatures. Ammonia, that is why, is synthesized at low temperatures;

$$N_2 + 3H_2 \rightleftharpoons 2NH_3; \qquad \Delta H^\circ = -92.4 \text{ kJ}$$

(b) Similarly for endothermic reaction where ΔH° is positive product formation would be favoured at elevated temperatures.

(c) For athermic reaction ($\Delta H^\circ = 0$); temperature has no effect on the product formation.

EXAMPLE 5.38 Calculate K_P for

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at 25°C if ΔG_f° of NH_3 (g) from its elements at standard state is -16.45 kJ mol^{-1}.

Solution Given that

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

where

$$\begin{aligned}\Delta G^\circ &= 2 \times \Delta G_f^\circ(NH_3, g) - \left[\Delta G_f^\circ(N_2, g) + 3\Delta G_f^\circ(H_2, g)\right] \\ &= 2(-16.45 \text{ kJ}) \\ &= -32.9 \text{ kJ}\end{aligned}$$

We also have

$$\Delta G^\circ = -RT \ln K_P \quad \text{or} \quad \ln K_P = -\frac{\Delta G^\circ}{RT}$$

Hence

$$\ln K_P = -\frac{-32.9 \text{ kJ}}{8.314 \times 10^{-3} \text{ kJ K}^{-1} \times 298 \text{ K}} = 13.28 \quad \text{or} \quad K_P = 5.85 \times 10^5 \quad \blacksquare$$

EXAMPLE 5.39 The value of K_P for the reaction

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

at 25°C is 9×10^2. Calculate the reaction Gibbs energy for the same reaction when the partial pressure of N_2 (g), H_2 (g) and NH_3 (g) are 0.32 bar, 0.73 bar and 0.98 bar, respectively.

Solution The reaction Gibbs energy

$$\Delta_r G = \Delta G^\circ + RT \ln \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}$$

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or

$$\Delta_r G = -RT \ln K_P + RT \ln \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}$$

$$= -8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln (9 \times 10^2)$$

$$+8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln \frac{0.98}{(0.32)^{1/2} (0.73)^{3/2}}$$

$$= -16853 \text{ J mol}^{-1} + 2531 \text{ J mol}^{-1}$$

$$= -14322 \text{ J mol}^{-1}$$

$$= -14.3 \times 10^3 \text{ J mol}^{-1}$$

Since $\Delta_r G$ is negative, the reaction is spontaneous in the forward direction. ■

EXAMPLE 5.40 The equilibrium constant K_P for

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at 25°C is 5.85×10^5. Calculate the value of K_P at 150°C if standard enthalpy of formation of NH_3 (g) is -46.11 kJ mol^{-1}.

Solution The given chemical equation is

$$N_2(g) + 3H_2^{\circ}(g) \rightleftharpoons 2NH_3(g)$$

where

$$\Delta H^{\circ} = 2\Delta H_f^{\circ}(NH_3, g) - 0 - 3 \times 0$$

$$= 2(-46.11) \text{ kJ}$$

$$= -92.22 \text{ kJ}$$

We also know

$$\frac{d \ln K_P}{dT} = \frac{\Delta H}{RT^2} \quad \text{or} \quad d \ln K_P = \frac{\Delta H}{RT^2} dT$$

Integrating between two temperatures T_1 and T_2 such that $T_2 > T_1$, we get

$$\int_{K_{P_1}}^{K_{P_2}} d \ln K_P = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

or

$$\ln \frac{K_{P_2}}{K_{P_1}} = -\frac{\Delta H}{R} \left(\frac{1}{T} \right)_{T_1}^{T_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

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or

$$\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

According to the present problem, we get

$$\ln \frac{K_{P_2}}{5.85\times10^5} = -\frac{92.22}{8.314\times10^{-3}}\left(\frac{1}{298} - \frac{1}{423}\right)$$

Here we consider ΔH remains constant in this temperature limit. Then

$$\ln \frac{K_{P_2}}{5.83\times10^5} = 11092\times9.92\times10^{-4} = 10.999 \quad \text{or} \quad K_{P_2} = 3.49\times10^{10}. \quad \blacksquare$$

5.24.6 Electro-chemical Cells

In this subsection, we shall take up the application of chemical potential to electro-chemical cells and show that equations like Nernst equation can be neatly arrived at from thermodynamic consideration based on the concept of chemical potentials. We will take up two representative examples: (i) the cells in which a chemical reaction is the source of the electromotive force (e.m.f.) and (ii) the cells in which the e.m.f. is on account of the concentration difference of electrolytes. The former are called *chemical cells* and the latter are called *concentration cells*.

Whatever may be the kind of cell, the e.m.f. of the cell is always on account of some transport process going on inside the cell, it may be a chemical reaction or a concentration difference driven transport, e.g. diffusion. The procedure underlying the thermodynamic derivation of the Nernst equation is simple. The free energy change of the transport process is equated to the net reversible work (in this case, electrical work) obtainable from the system. If e.m.f of a reversible cells is E, and the process taking place within it is accompanied by the passage of n faradays of electricity, i.e. nF coulombs, the work done by the cell is nEF. Since, as shown earlier, decrease in free energy of a process is equal to the net reversible work obtainable from the system (excluding pressure volume work) we can write for the present case,

$$\Delta G = -nEF \tag{5.229}$$

Chemical cells

As a typical example let us consider the following cell

$$\mathrm{Zn(s)}\left|\mathrm{Zn^{++}(aq)}\right\|\mathrm{Cu^{++}(aq)}\left|\mathrm{Cu(s)}\right. \tag{A}$$

The convention followed in writing the above cell are the usual ones. The more negative half-cell is written on the left-hand side and the two parallel lines denote that the direct junction between the two electrolytic solutions has been avoided. It is assumed that the student has done the elementary course in physical chemistry and is familiar with the conventions used in writing the electro-chemical cells.

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Since the Zn (s) | Zn^{++} (aq) half-cell is more negative it should be source of electrons in the external circuit. Hence the equilibrium prevailing in the half-cell would be

$$Zn\,(s) \rightleftharpoons Zn^{++}(aq) + 2e \tag{5.230}$$

The two electrons generated in the above process would flow through the external circuit from left to right and would be consumed by the copper ions. Therefore, on the right side, we would have the following process:

$$Cu^{++}(aq) + 2e \rightleftharpoons Cu(s) \tag{5.231}$$

The total process going on in the cell can be written by adding up Equations (5.230) and (5.231). The total process therefore would be

$$Zn(s) + Cu^{++}(aq) \rightleftharpoons Zn^{++}(aq) + Cu(s) \tag{5.232}$$

In the chemical reaction (5.232) transfer of 2 moles of electrons is involved, i.e. the process takes place for the passage of 2 faradays of electricity. The free energy change for the reaction (5.232) can be written as

$$\Delta G = \left(\mu_{Zn^{++}} + \mu_{Cu}\right) - \left(\mu_{Zn} + \mu_{Cu^{++}}\right) \tag{5.233}$$

Using the definition $\mu_i = \mu_i^0 + RT \ln a_i$, where a_i represents the activity, Equation (5.233) can be transformed to read

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{Zn^{++}} a_{Cu}}{a_{Cu^{++}} a_{Zn}} \tag{5.234}$$

Using Equation (5.229), Equation (5.234) can be transformed into

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{Zn^{++}} a_{Cu}}{a_{Cu^{++}} a_{Zn}} \tag{5.237}$$

where E° is the standard e.m.f of the cell. Since activities of copper and zinc in their pure metallic form can be taken to be unity we can rewrite Equation (5.237) in the form

$$E = E^\circ - \frac{RT}{2F} \frac{a_{Zn^{++}}}{a_{Cu^{++}}} \tag{5.238}$$

which is well-known *Nernst equation* for the cell (A). For the general reaction

$$aA + bB + \cdots \rightleftharpoons lL + mM + \cdots$$

going on in a chemical cell for the passage of n faradays of electricity, the Nernst equation can be written as

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_L^l a_M^m \cdots}{a_A^a a_B^b \cdots} \tag{5.239}$$

Concentration cells

Consider the following cell

$$Ag\,(s) \,|\, Ag\,(0.01\ M) \,||\, Ag\,(0.1\ M) \,|\, Ag\,(s) \qquad . \quad (B)$$

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The vertical parallel lines indicate that the junction between the two liquid has been eliminated.

In writing cell (B) the same conventions have been followed as were followed in the case of cell (A). Since the half-cell written in the left-hand side is more negative, it should be the source of electrons. Hence on the left-hand side, the following reaction should occur:

$$\text{Ag (s)} \rightleftharpoons \text{Ag}^+ \text{ (0.01 M)} + e \tag{5.240}$$

The electron thus generated should flow in the external circuit from left to right and should be consumed there. Therefore, the process on the right-hand side half, the cell should be

$$\text{Ag}^+ \text{ (0.1 M)} + e \rightleftharpoons \text{Ag} \tag{5.241}$$

The total process can be written by adding up Equations (5.240) and (5.241). Thus, we have

$$\text{Ag}^+ \text{ (0.1 M)} \rightleftharpoons \text{Ag}^+ \text{ (0.01 M)} \tag{5.242}$$

The net process, therefore, is the transfer of silver ions from higher concentration to lower concentration. In this process transfer of one mole of electrons is involved. In other words, this process takes place for the passage of one faraday of electricity. The free energy change for the process (5.242) can be written as

$$\Delta G = \left[\mu_{\text{Ag}^+}(0.01 \text{ M}) - \mu_{\text{Ag}^+}(0.1 \text{ M})\right] \tag{5.243}$$

Using the definition $\mu_i = \mu_i^\circ + RT \ln a_i$, Equation (5.243) can be written as

$$\Delta G = \left[\mu^0_{\text{Ag}^+} + RT \ln a_{\text{Ag}^+}(0.01 \text{ M})\right] - \left[\mu^0_{\text{Ag}^+} + RT \ln a_{\text{Ag}^+}(0.1 \text{M})\right]$$

$$= R \ln \frac{a_{\text{Ag}^+}(0.01 \text{ M})}{a_{\text{Ag}^+}(0.1 \text{ M})} \tag{5.244}$$

Since $\Delta G = -EF$, we have from Equation (5.244)

$$E = \frac{RT}{F} \ln \frac{a_{\text{Ag}^+}(0.1 \text{ M})}{a_{\text{Ag}^+}(0.01 \text{ M})} \tag{5.245}$$

which is the Nernst equation for the concentration cell (B).

EXAMPLE 5.41 Calculate ΔG° and equilibrium constant K at 25°C for the reaction occurring in the following cells:

(i) $\text{Zn (s)}|\text{ZnCl}_2\text{ (aq)}\|\text{CdSO}_4\text{ (aq)}|\text{Cd (s)}$

(ii) $\text{Cd (s)}|\text{CdSO}_4\text{ (aq)}, \text{Hg}_2\text{SO}_4\text{ (s)}|\text{Hg (l)}$

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Given standard reduction potentials:

$$E^{\circ}_{Zn^{+2}/Zn} = -0.7618 \text{ volt}$$

$$E^{\circ}_{Cd^{+2}/Cd} = -0.403 \text{ volt}$$

$$E^{\circ}_{Hg_2SO_4(s),\ SO_4^{-2}/Hg\ (l)} = +0.6141 \text{ volt}$$

Solutions (i) Half-cell reactions are:

$$Zn(s) \rightarrow Zn^{+2}(aq) + 2e$$

$$Cd^{+2}(aq) + 2e \rightarrow Cd(s)$$

Total cell reaction is

$$Zn(s) + Cd^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cd(s)$$

where

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -2 \times 96500 \text{ coulomb mol}^{-1} \times E^{\circ}_{cell} \text{ volt}$$

and

$$E^{\circ}_{cell} = E^{\circ}_{red}(\text{at positive electrode}) - E^{\circ}_{red}(\text{at negative electrode})$$

$$= -0.403 - (-0.7618)$$

$$= 0.3588 \text{ volt}$$

Then

$$\Delta G^{\circ} = -2 \times 96500 \text{ coulomb mol}^{-1} \times 0.3588 \text{ volt}$$

$$= -69248.4 \text{ coulomb mol}^{-1} \times \text{volt}$$

$$= -69248.4 \text{ J mol}^{-1}$$

$$= -69.2484 \text{ kJ mol}^{-1}$$

We also have

$$\Delta G^{\circ} = -RT \ln K$$

Then

$$\ln K = -\frac{\Delta G^{\circ}}{RT} = \frac{69.2484 \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ k JK}^{-1} \text{ mol}^{-1} \ 298 \text{ K}} = 27.95$$

Thus

$$K = 1.38 \times 10^{12}$$

(ii) Half-cell reactions are:

$$Cd\ (s) \rightarrow Cd^{+2}(aq) + 2e$$

$$Hg_2SO_4\ (s) + 2e \rightarrow 2Hg\ (l) + SO_4^{-2}(aq)$$

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Total cell reaction is

$$Cd(s) + Hg_2SO_4(s) \rightarrow Cd^{+2}(aq) + 2Hg(\ell) + SO_4^{-2}(aq)$$

where

$$\Delta G^\circ = -nFE^\circ_{cell}$$

and

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red} \text{ (at positive electrode)} - E^\circ_{red} \text{ (at negative electrode)} \\ &= 0.6141 - (-0.403) \\ &= 1.0171 \text{ volt} \end{aligned}$$

Then

$$\begin{aligned} \Delta G^\circ &= -2 \times 96500 \text{ coulomb mol}^{-1} \times 1.0171 \text{ volt} \\ &= -196.3 \text{ kJ mol}^{-1} \end{aligned}$$

We also have

$$\Delta G^\circ = -RT \ln K$$

Then

$$\ln K = -\frac{\Delta G^\circ}{RT} = \frac{196.3 \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ mol}^{-1} \times 298 \text{ K}} \quad \text{or} \quad K = 7.65 \times 10^{33} \qquad \blacksquare$$

EXAMPLE 5.42 Calculate the e.m.f. of the the cell:

$$\text{Zn (s)} \left| \begin{matrix} \text{ZnCl}_2 \text{ (soln)} \\ (m = 0.02, \gamma = 0.65) \end{matrix} \right| \text{AgCl (s)} \left| \text{Ag} - \text{Ag} \right| \text{AgCl (s)} \left| \begin{matrix} \text{ZnCl}_2 \text{ (soln)} \\ (m = 1.5, \gamma = 0.29) \end{matrix} \right| \text{Zn (s)}$$

1 2

Solution This is an example of concentration cell without transference. The cell reaction in the first compartment (1):

$$Zn(s) \rightarrow Zn^{+2}(aq) + 2e$$

$$2AgCl(s) + 2e \rightarrow 2Ag(s) + 2Cl^-$$

Combining them, we get

$$Zn(s) + 2AgCl(s) \rightarrow 2Ag(s) + ZnCl_2(a_1)$$

Similarly, the cell reaction in the second compartment (2):

$$2Ag(s) + 2Cl^-(aq) \rightarrow 2AgCl(s) + 2e$$

$$Zn^{+2}(aq) + 2e \rightarrow Zn(s)$$

Combining them, we get

$$2Ag(s) + ZnCl_2(a_2) \rightarrow Zn(s) + 2AgCl(s)$$

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Therefore, the overall cell reaction in the above cell is

$$ZnCl_2(a_2) \rightarrow ZnCl_2(a_1)$$

Cell e.m.f. for compartment 1 is

$$E_1 = E^\circ_{cell} - \frac{RT}{2F} \ln a_1$$

Cell e.m.f. for compartment 2 is

$$E_1 = E^{\circ\prime}_{cell} - \frac{RT}{2F} \ln \frac{1}{a_2} = -E^\circ_{cell} - \frac{RT}{2F} \ln \frac{1}{a_2}$$

Therefore, the overall cell e.m.f. of above cell is

$$E = E_2 + E_1$$

$$= -\frac{RT}{2F} \ln \frac{1}{a_2} - \frac{RT}{2F} \ln a_1$$

$$= -\frac{RT}{2F}\left(\ln \frac{1}{a_2} + \ln a_1\right)$$

$$= -\frac{RT}{2F} \ln \frac{a_1}{a_2}$$

$$= \frac{RT}{2F} \ln \frac{a_2}{a_1}$$

$$= \frac{RT}{2F} \ln \frac{m_2^3 \gamma_2^3}{m_1^3 \gamma_1^3}$$

[Here γ = mean ionic activity coefficient]

$$= \frac{8.314 \times 298 \times 3}{2 \times 96,487} \times 2.303 \log \frac{1.50 \times 0.29}{0.02 \times 0.65}$$

$$= 0.0888 \log \frac{0.435}{0.013}$$

$$= 0.1354 \text{ volt} \quad \blacksquare$$

EXAMPLE 5.43 Calculate the e.m.f. of the cell

$$H_2(g, 1\,atm) \left| \begin{matrix} HCl(aq) \\ m = 0.02,\ \gamma = 0.88 \end{matrix} \right| \left| \begin{matrix} HCl(aq) \\ m = 1.00,\ \gamma = 0.81 \end{matrix} \right| H_2(g, 1\ atm)$$

Solution This is an example of concentration cell with transference. Two hydrogen electrodes are dipped in two different concentrations of hydrochloric acid solution. The cell reaction at left electrode is

$$\frac{1}{2}H_2(g, 1\ atm) \rightarrow H^+(a_1) + e$$

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and at right, the electrode is

$$H^+(a_2) + e \rightarrow \frac{1}{2}H_2(g, 1\ atm)$$

The overall reaction is

$$H^+(a_2) \rightarrow H^+(a_1) \cdots \quad (1)$$

In the external circuit electrons flow from left to right. Therefore to complete the circuit electrons or more accurately Cl^- ions move from right to left through the liquid junction. If t_- is the transference number of Cl^-, then for every faraday passing through the cell t_- equivalents of Cl^- ions will pass from a solution of activity a_2 to a solution of activity a_1. Therefore,

$$t_-Cl^-(a_2) = t_-Cl^-(a_1) \quad (2)$$

t_+ or $(1 - t_-)$ equivalent of H^+ ions will pass from a solution of activity a_1 to a solution of activity a_2. Therefore,

$$(1-t_-)H^+(a_1) = (1-t_-)H^+(a_2) \quad (3)$$

Adding Equations (1), (2) and (3), we get

$$H^+(a_2) + t_-Cl^-(a_2) + (1-t_-)H^+(a_1) = H^+(a_1) + t_-Cl^-(a_1) + (1-t_-)H^+(a_2)$$

or

$$t_-H^+(a_2) + t_-Cl^-(a_2) = t_-H^+(a_1) + t_-Cl^-(a_1)$$

or

$$t_-HCl(a_2) = t_-HCl(a_1) \quad (4)$$

Hence

$$E_{cell} = -\frac{RT}{F}\ln\frac{a_1^{t_-}}{a_2^{t_-}} = -\frac{t_-RT}{F}\ln\frac{a_1}{a_2}$$

or

$$E_{cell} = -\frac{t_-RT}{F}\ln\frac{(m_1\gamma_1)^2}{(m_2\gamma_2)^2} = -\frac{2t_-RT}{F}\ln\frac{m_1\gamma_1}{m_2\gamma_2}$$

Here γ = mean ionic activity coefficient. Then

$$E_{cell} = -\frac{2\times0.178\times8.314\times298}{96,487}\times2.303\ \log\ \frac{0.02\times0.88}{1\times0.81} = 0.351\ volt \quad \blacksquare$$

Heat of reaction from e.m.f. data

The e.m.f. E of a reversible cell which is related to ΔG for the reaction occurring within it for the passage of n faraday's of electricity, at constant temperature and pressure, is given by the equation: $\Delta G = -nEF$. Using this equation in the Gibbs–Helmholtz equation, we get

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$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

or

$$\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] \tag{5.246}$$

Equation (5.246) gives us a convenient method for the determination of the heats of reaction from e.m.f. data.

EXAMPLE 5.44 For a standard cadmium cell

$$E = 1.01463 \text{ volts at } 25°C, \quad n = 2 \quad \text{and} \quad \left(\frac{\partial E}{\partial T}\right)_P = -5.0\times10^{-5} \text{ VK}^{-1}$$

Calculate the values of ΔG, ΔS and ΔH for the reaction that goes on within the cadmium cell.

Solution We have

$$\begin{aligned}\Delta G &= -nEF \\ &= -2\times1.01463\times96500 \\ &= -195815 \text{ volt coulomb} \\ &= -195815 \text{ J}\end{aligned}$$

and

$$\begin{aligned}\Delta S &= -\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \\ &= nF\left(\frac{\partial E}{\partial T}\right)_P \\ &= 2\times96500\times\left(-5.0\times10^{-5}\right) \\ &= -9.65 \text{ coulomb volt K}^{-1} \\ &= -9.65 \text{ JK}^{-1}\end{aligned}$$

Therefore,

$$\begin{aligned}\Delta H &= -nEF + nFT\left(\frac{\partial E}{\partial T}\right)_P \\ &= \Delta G + T\Delta S \\ &= -195815 + (298)(-9.65) \\ &= -198691 \text{ J}\end{aligned}$$

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After having discussed some of the representative applications of the concept of chemical potential, we close this chapter and pass on to the thermodynamics of open systems. But before we do that it is desirable to touch upon the third law of thermodynamics for the sake of completeness. ■

5.25 THE THIRD LAW OF THERMODYNAMICS

We have already recorded the statement of the third law of thermodynamics, in this chapter, while dealing with the Carnot engine. Let us repeat the statement once again, "It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to the absolute zero in finite number of operations".

To illustrate the above statement let us consider the case of cooling by adiabatic demagnetization. This technique of producing low temperatures was independently proposed by Giauque and Debye. The proposal was experimentally realized by Giauque. Certain salts particularly of rare earths have high paramagnetic susceptibilities. The cations behave like small magnets and line up in the direction of an external magnetic field, i.e. the salt is magnetized. When the field is removed, the alignment of the small magnet disappears, i.e. the salt is demagnetized. While magnetizing, the substance was also cooled using liquid helium in outer jacket of the vessel in which the substance was kept. The liquid helium was then withdrawn leaving the chilled magnetized substance thermally isolated from its environment by the adiabatic barrier of the evacuated space. The magnetic field was then withdrawn to bring about adiabatic demagnetization. Though the demagnetization is not strictly reversible but no serious error is caused if it is considered to be so. For reversible adiabatic demagnetization $\Delta S = 0$. The experiment of Giauque is represented in Figure 5.14 on a T-S plane. The two curves shown in the Figure 5.14 are for demagnetized state ($H = 0$) and for the magnetized state ($H = H_i$).

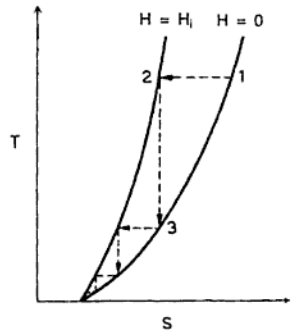

Figure 5.14 Adiabatic demagnetization on a T-S plane.

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At constant temperature, the transition from demagnetized state is from a state of higher entropy and energy to a state of lower entropy and energy—the transition $1 \rightarrow 2$ in Figure 5.14 represents the transition. When the magnetic field is reduced to zero there is an isentropic change in the system back to the curve corresponding to $H = 0$. This is shown by the transition $2 \rightarrow 3$ in Figure 5.14. It is now obvious from Figure 5.14 that these transitions should bring about a fall in temperature. At first sight, it would appear that by performing such transitions successively it should be possible to attain absolute zero of temperature while actually it is not so. A perusal of Figure 5.14 reveals that the amount of cooling achieved in each successive operation (isothermal magnetization followed by adiabatic demagnetization) goes on decreasing. Thus even if perfect reversibility could be achieved, the absolute zero would be attained only in the limit of infinite series of such steps (isothermal magnetization followed by adiabatic demagnetization). For isothermal magnetization step, $T \rightarrow 0$, as $\Delta S_0 \rightarrow 0$ (Figure 5.14). In fact, there is nothing special about the magnetization case, any cooling procedure can be reduced to a T–S diagram of the type shown in Figure 5.14. Generalizing we can say that for any isothermal reversible process, say $a \rightarrow b$ the third law requires that in the limit as $T \rightarrow 0$, $S_0^a \rightarrow S_0^b$ or $\Delta S_0 \rightarrow 0$. This statement of the third law is similar to the famous Nernst heat theorem which states that "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances".[6] This statement is helpful in estimating the absolute values of entropies. We know that

$$dS = \frac{C_P}{T} dT$$

which on integration yields

$$\int_0^T dS = \int_0^T \frac{C_P}{T} dT$$

or

$$S_T - S_0 = \int_0^T \frac{C_P}{T} dT \tag{5.247}$$

The right-hand side of Equation (5.247) can be easily evaluated. The only problem in estimating the absolute value of entropy at temperature T (i.e. S_T) is that what value should be assigned to S_0. Although the Nernst heat theorem is only for the perfect crystalline substances, Max Planck proposed that entropies of all pure chemical compounds in their stable states at 0 K can also be taken to be zero. This proposal is equivalent to setting the constant $S_0 = 0$.

6. This statement was made by Lewis and Randall.

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QUESTIONS

1. Carnot engine is a highly non-realistic device. List a few points because of which it is non-realistic.
2. What is Carnot's theorem? What is the message driven home from this theorem?
3. What is the lowest temperature conceivable according to Carnot's engine and why?
4. What is absolute zero of temperature according to Carnot's engine?
5. What is the value of entropy change in one Carnot's cycle?
6. The equation $(dS)_{u,v} = 0$ represents the condition of equilibrium in an isolated system. Does it represent that at equilibrium (i) entropy maximizes (ii) entropy minimizes (iii) neither of the two, remains steady?
7. The equation $(dU)_{s,v} = 0$ also represents the condition of equilibrium in an isolated system. Does it represent that at equilibrium (i) U minimizes (ii) U maximizes (iii) neither of the two, remains steady?
8. The equation $(dG)_{T,P} = 0$ represents the condition of equilibrium under table top conditions. Does it represent that at equilibrium (i) G maximizes (ii) G minimizes (iii) neither of the two happens—it remains steady?
9. Why is "free energy" called free energy? The adjective "free" indicates what freedom?
10. One mole of oxygen has been mixed with another one mole of oxygen at the same temperature and pressure. What would be the value of entropy of mixing? Explain why?
11. For a certain chemical equilibrium say $aA + bB + \cdots \rightleftharpoons lL + mM + \cdots$ the value of standard free energy change is zero at a certain temperature. What would be the value of equilibrium constant at the temperature?
12. The three phases (solid, liquid, and vapour) of water at a given pressure (atmospheric pressure) can be at equlibrium at one and only one temperature. Rationalize this statement on the basis of phase rule.
13. In a closed system maintained under adiabatic conditions entropy increases because of a certain process. Can this process be reversed? If not why?
14. The e.m.f. of a certain chemical cell does not vary with temperature. Should the heat of cell reaction vary with temperature? If not why?
15. An inventor claims to have perfected an engine which extracts energy from water boiling at 100°C. The engine after doing work rejects the remaining energy to the sink which is melting ice at 0°C. He claims that the efficiency of energy conversion is 50%. Should his claim be accepted? If not why?

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EXERCISES

5.1 If the temperature of a heat source is 600 K and that of a heat sink is 400 K, calculate the maximum thermal efficiency of the heat engine.

5.2 Calculate the Carnot efficiency of a steam engine operating on steam at 100°C and discharging at 50°C.

5.3 Prove that all reversible engines are equally efficient those are working between the same temperature difference.

5.4 Calculate the molar entropy change when an ideal gas expands isothermally and reversibly from an initial volume of 1 L to a final volume of 2 L at 298 K.

5.5 Calculate the molar entropy change when neon gas is heated from 35°C to 235°C at constant volume. Given C_V of neon gas = 29.1 JK^{-1} mol^{-1}.

5.6 Calculate the change in entropy when 100 g of water is heated from 25°C to 200°C under constant atmospheric pressure. Given that heat capacity of liquid water is 75.29 JK^{-1} mol^{-1}, heat capacity of water vapour (18.5 + 0.497) JK^{-1} mol^{-1} and enthalpy of vaporization is 44 kJ mol^{-1}.

5.7 Three black balls and one white ball are collected in the neck of an inverted Maxwell Demon bottle one over the other. Consider that black balls have unit mass each and white ball is massless spacer.

(a) Calculate the total number of possible configuration.
(b) If all configurations are equally probable then calculate probability of getting a configuration.
(c) If one energy level can have only one ball and energy levels are 0, 1, 2 ..., then calculate the total energy and average energy of the system.
(d) If the lower level of the neck of the inverted bottle is raised one energy level up then calculate the change in the energy of the system.

5.8 Calculate the relative number of distinguishable quantum states in water–vapour and in water at 100°C. Given ΔH_{vapour} = 44 kJ mol^{-1} at 100°C and Boltzmann constant $k = 1.38 \times 10^{-23}$ JK^{-1}.

5.9 Four moles of an ideal gas expands isothermally and reversibly at 25°C from an initial volume of 1 L to a final volume of 5 L. Calculate the change in work function of the process.

5.10 One mole of an ideal gas expands isothermally at 25°C from an initial pressure of 225 kPa to a final pressure of 50 kPa. Calculate both ΔG and ΔS.

5.11 Standard enthalpy of combustion of methane gas is –890 kJ and standard entropy change for the same combustion is –242.98 JK^{-1} at 25°C. Calculate ΔA and ΔG of the reaction. How much energy can be extracted as work?

5.12 Calculate the change in entropy when a mole of an ideal gas is compressed from 600 cm^3 to 200 cm^3 and simultaneously the temperature of the gas is increased from 25°C to 100°C. Consider that $C_V = (3/2)R$.

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5.13 For the reaction

$$2CO\,(g) + 2NO\,(g) = N_2\,(g) + 2CO_2\,(g), \quad \Delta S = -197.77\ JK^{-1}$$

at 25°C. The standard heat of formation of CO (g), NO (g), N_2 (g) and CO_2 (g) are –110.53, 90.25, 0.0 and –393.51 kJ mol^{-1}, respectively. Will the reaction be spontaneous at 25°C.

5.14. The standard reaction enthalpy ($\Delta_r H°$) for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at 25°C is –92.22 kJ mol^{-1}. What is the change in entropy of the surroundings at 25°C when the reaction takes place at constant pressure?

5.15 The standard entropy change for the reaction

$$C_3H_6\,(g) + \frac{9}{2}O_2\,(g) \rightarrow 3CO_2\,(g) + 3H_2O\,(l) \text{ is } -339.23\ JK^{-1}$$

at 25°C. Calculate the standard reaction enthalpy if the standard Gibbs energy of formation of C_3H_6 (g), CO_2 (g) and H_2O (l) are 62.78, –394.36 and –237.13 kJ mol^{-1}, respectively.

5.16 Calculate the inversion temperature of carbon dioxide gas if the van der Waals' constants $a = 3.6$ litre^2 – atm mol^{-2} and $b = 4.3 \times 10^{-2}$ litre mol^{-1} and the gas constant $R = 0.082$ L atm K^{-1} mol^{-1}.

5.17 Find out the boiling temperature of water when the barometric pressure is 0.7 bar. Given enthalpy of vaporization of water = 40.66 kJ mol^{-1}.

5.18 The vapour pressure of a pure carbon tetrachloride at 10°C and 50°C are respectively 0.075 bar and 0.422 bar. Calculate the normal boiling point of carbon tetrachloride and its molar enthalpy of vaporization.

5.19 Calculate the maximum energy that can be extracted as (i) heat and (ii) non-expansion work for the formation of liquid water from H_2 (g) and O_2 (g), i.e.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$$

if standard enthalpy of formation of H_2O (l) from its element is –285.83 kJ mol^{-1} and standard Gibbs energy of formation of H_2O(l) is –237.13 kJ mol^{-1}.

5.20. The vapour pressure of pure benzene at 61°C is 400 torr. When 0.13 g of a solute is dissolved in 5 g of benzene then the vapour pressure of solvent over the solution is 386 torr. Calculate the molar mass of the solute.

5.21. The vapour pressure of pure carbon disulphide at 20°C is 11.386 kPa. When 2 g of sulphur is dissolved in 100 g of carbon disulphide then the vapour pressure becomes 11.319 kPa. Calculate the molar mass of sulphur.

5.22. Estimate the elevation of boiling point of a solution, which is made by dissolving 50 g of sucrose in 100 g of water. Given K_b of water = 0.51 Kkg mol^{-1}.

5.23 The depression of freezing point of a solution made by dissolving a solute in water is 0.2 K. Calculate the mole fraction of solute in solution if the enthalpy of fusion of water is 6.01 kJ mol^{-1}.

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5.24 Write half cell-reactions and overall cell-reaction for each of the following cells:

(i) $Ag\,(s)|AgI\,(s), I^-(aq)||Cl^-\,(aq), AgCl\,(s)|Ag\,(s)$

(ii) $Zn\,(s)|Zn^{+2}\,(aq)||SO_4^{-2}\,(aq), PbSO_4\,(s)|Pb\,(s)$

(iii) $Ag\,(s)|AgCl\,(s), Cl^-\,(aq)|Cl_2\,(g, 1\text{ atm})|Pt\,(s)$

5.25 Calculate $\Delta G°$ and equilibrium constant K at 25°C of the reaction occurring in the following cells.

(i) $Pt(s)|Fe^{+2}\,(aq), Fe^{+3}\,(aq)||MnO_4^-(aq), H^+(aq), Mn^{+2}\,(aq)|Pt\,(s)$

(ii) $Pb\,(s)|Pb^{+2}\,(aq)||Cu^{+2}\,(aq)|Cu\,(s)$

Given

$$E°_{Fe^{+3}/Fe^{+2}} = 0.77,\ E°_{MnO^{-4},H^+/Mn^{+2}} = 1.51\text{ V}$$

$$E°_{Pb^{+2}/Pb} = -0.13,\ \text{and}\ E°_{Cu^{+2}/Cu} = 0.34$$

5.26 Construct a cell using following two electrodes, write overall cell reaction, calculate $E°_{cell}$.

$$Pt\,(s)|Cl_2\,(g)\,|Cl^-\,(aq);\quad E°_{Cl_2/Cl^-} = 1.3595,$$

$$Hg\,(l)|Hg_2Cl_2\,(s), Cl^-\,(aq);\quad E°_{Cl^-,Hg_2Cl_2/Hg} = 0.268$$

5.27 Write cell reaction and calculate cell e.m.f. of the following cell:

$$Pt\,(s)|Cl_2\,(g, P = 0.2\text{ atm})|NaCl\,(\text{solution})|Cl_2\,(g,\ P = 1\text{ atm})|Pt\,(s)$$

5.28 Write cell reaction and calculate cell e.m.f. of the following cell:

$$Zn\,(s)|Zn^{+2}\,(a = 0.05)||Fe^{+3}\,(a = 0.2),\ Fe^{+2}\,(a = 0.02)|Pt\,(s)$$

$$\text{Given } E°_{Zn^{+2}/Zn} = -0.7618\text{V},\ E°_{Fe^{+3}/Fe^{+2}} = 0.771\text{ V}$$

5.29 Find the cell reaction and calculate the potential of the cell:

$$Cd(s)\left|\begin{matrix}CdSO_4\\(m = 0.01,\ \gamma = 0.383)\end{matrix}\right|PbSO_4\,(s)\left|Pb - Pb\right|PbSO_4\,(s)\left|\begin{matrix}Cd\,SO_4\\(m = 1.00,\ \gamma = 0.042)\end{matrix}\right|Cd\,(s)$$

5.30. Write the cell reaction and calculate the cell potential of the following cell with transference:

$$Pb(s)\left|PbSO_4\,(s)\right|\begin{matrix}CuSO_4\\(m = 0.2,\ \gamma = 0.110)\end{matrix}\left|\begin{matrix}CuSO_4\\(m = 0.02,\ \gamma = 0.320)\end{matrix}\right|PbSO_4\,(s)\left|Pb(s)\right.$$

The transport number of Cu^{+2} is 0.370. Is the cell reaction spontaneous as written?

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Chapter 6

The Question of Ideality

It is well known that ideal situations do not belong to the real world. Concepts like, equilibrium, reversibility, perfect gas, etc., represent highly idealized situations. Ideality resides only in one's imagination and one can tend to ideality only in limits. These facts, notwithstanding, ideality has invariably been invoked in science. This has been done for convenience. The ideal situations can be conveniently handled using simple mathematical apparatus. The usual practice has been first to consider the ideal situation and then introduce corrections in the treatment to account for the behaviour of the real situation. In this chapter we propose to demonstrate this by considering the case of gases and liquids (solutions).

6.1 THE CASE OF GASES

The ideal gas model makes several postulates, which are unacceptable prima facie. For example, (i) molecules are considered as point masses, i.e. practically having no volume, (ii) there are no forces of attraction and repulsion existing between the molecules, (iii) the collisions between the molecules are elastic collisions and so on. Based on this model the following equation of state for n moles of an ideal gas is arrived at:

$$PV = nRT \tag{6.1}$$

The result is obvious: there is hardly a gas that obeys Equation (6.1) (see Figure 3.5); at the most Equation (6.1) can be made to conform to the experimental results only in the limits, i.e. low pressure and high temperatures. Thus ideal gas is a non-existent gas; it is just a fanciful concept. Many attempts have been made to modify the ideal equation of state: Equation (6.1), and change it into a form that would represent *P-V-T* data on real gases. Corrections had to be introduced both for the pressure as well as the volume and often two or more constants entered into the equations. Of the several equations of state proposed for real gases on empirical or semiempirical basis, two most widely used are (i) the virial equation and (ii) the van der Waals equation.

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6.1.1 Virial Equation

The virial equation can be written as

$$PV = RT\left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \cdots\right] \tag{6.2}$$

The coefficients $B(T)$, $C(T)$, etc., are called second, third, etc., virial coefficients and are functions of temperature T. Virial coefficients are used in several situations, for example, in the theory of solutions. The virial equation is also the basis for theoretical calculations from statistical models of non-ideal gases, in which it turns out that $B(T)$ represents the deviation from ideality due to interactions between pairs of molecules.

The ratios of P, V and T to the critical values P_C, V_C and T_C respectively, are called *reduced pressure* P_R, *reduced volume* V_R and *reduced temperature* T_R, i.e.

$$P_R = \frac{P}{P_C}; \quad V_R = \frac{V}{V_C}; \quad T_R = \frac{T}{T_C} \tag{6.3}$$

P_C, V_C, T_C are definite quantities for a particular gas. Therefore, P_R, V_R, T_R are some numbers indicating how many times the critical values are greater or smaller than the given P, V and T.

van der Waals pointed out that, to a fairly good approximation at moderate pressures, all gases follow the same equation of state in terms of reduced variables. Thus $V_R = F(P_R, T_R)$, where F would be the same function for all the different gases studied. van der Waals called this rule the *principle of corresponding states*. The principle of corresponding states is, nevertheless important, since it shows that deviation of a gas from ideality is not determined by the absolute values of P, V, T but by the reduced values P_R, V_R, T_R which take into account the nature of the actual gas.

A convenient way to summarize P-V-T data for real gases is to introduce a compressibility factor Z, such that $Z = PV/(nRT)$. Chemical engineers concerned with the properties of gases at elevated pressures have prepared graphs to show the variation of Z with P and T and they have found to a good approximation even at fairly high pressure, that Z appears to be a universal function of the reduced variables, P_R and T_R,

$$Z = F(P_R, T_R) \tag{6.4}$$

This behaviour is illustrated in Figure (6.1) for a number of different gas, where the compressibility factor Z is plotted at various reduced temperatures against the reduced pressure. At these moderate pressures the data fit well. The curves in Figure 6.1 illustrate the law of corresponding states.

6.1.2 van der Waals Equation

van der Waals equation is the most widely used equation of state for real gases. In deducing this equation of state the two prima facie unacceptable postulates of ideal gas model were modified. Instead of treating molecules of the gas as point

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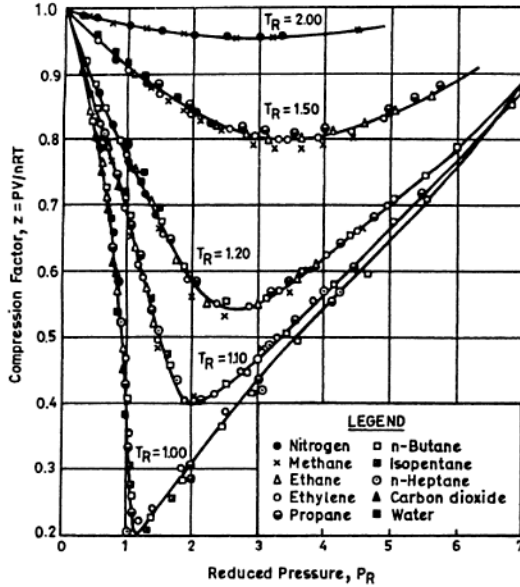

Figure 6.1 Compressibility factor as a function of reduced variables. [Su, Gouq-Jen, *Ind. Eng. Chem.* 38 (1946) 803.]

masses they were treated as rigid spheres of finite diameter. Further instead of saying that no forces exist between molecules, it was assumed that they exert attractive forces on one another. In Figure 6.2 main features of the van der Waals model are depicted.

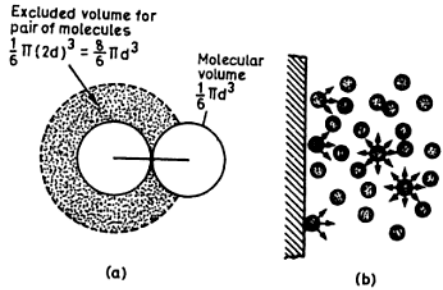

Figure 6.2 van der Waals correction to the ideal gas model: (a) excluded volume (b) intermolecular forces.

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The nearest approach of the centre of one molecule to the centre of another molecule of the same species is d. Thus for each pair of molecule a volume of $(4/3)\pi d^3 = 8v_m$ is excluded from the total gas-volume V of n moles, where v_m is the molecular volume. The volume excluded for one molecule is $4v_m$. The total excluded volume for nL molecules, L being the Avogadro number, is thus $nL(4v_m) = nb$, where b is a constant for a given species of gas. In view of this correction, the ideal gas equation gets modified to

$$P(V - nb) = nRT \tag{6.5}$$

Equation (6.5) is useful at high temperature and high pressure, where the excluded volume is more important than the effect of intermolecular forces.

The correction for attractive forces was made in the following way. Since attraction occurs between pairs of molecues, it must increase as the square of the concentration $(n/V)^2$. The actual pressure (P) will be less than the ideal gas pressure by an amount $a(n/V)^2$, where a is a different constant for each gas. The result of both the van der Waals correction is, therefore

$$\left[P + a\left(\frac{n}{V}\right)^2\right](V - nb) = nRT \tag{6.6}$$

The van der Waals equation, Equation (6.6), represents the P-V-T behaviour of gases quite well when they deviate moderately from ideal behaviour.

EXAMPLE 6.1 Express critical constants (P_C, V_C and T_C) in terms of van der Waals constants a, b.

Solution It can be observed that in P-V isothermal for a van der Waals gas, maxima and minima coalesce at the critical point. Below critical temperature, maxima and minima are observed, but above critical temperature, they vanish. Therefore,

$$\left(\frac{dP}{dV}\right)_T \quad \text{and} \quad \left(\frac{d^2P}{dV^2}\right)_T$$

become zero at critical temperature. The van der Waals equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1}$$

Therefore,

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{2}$$

or

$$\left(\frac{dP}{dV}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3} \tag{3}$$

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and

$$\left(\frac{d^2P}{dV^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \tag{4}$$

Therefore at critical temperature,

$$\frac{RT_C}{(V_C-b)^2} = \frac{2a}{V_C^3} \tag{5}$$

and

$$\frac{2RT_C}{(V_C-b)^3} = \frac{6a}{V_C^4} \tag{6}$$

Dividing equation (5) by (6) we get

$$\frac{V_C-b}{2} = \frac{V_C}{3} \quad \text{or} \quad V_C = 3b \tag{7}$$

From equation (5),

$$\frac{RT_C}{(3b-b)^2} = \frac{2a}{(3b)^3} \quad \text{or} \quad \frac{RT_C}{4b^2} = \frac{2a}{27b^3}$$

or

$$T_C = \frac{8a}{27Rb} \tag{8}$$

From equation (2),

$$P_C = \frac{RT_C}{V_C-b} - \frac{a}{V_C{}^2}$$

or

$$P_C = \frac{R}{(3b-b)}\frac{8a}{27Rb} - \frac{a}{(3b)^2}$$

or

$$P_C = \frac{a}{27b^2} \quad \blacksquare \tag{9}$$

EXAMPLE 6.2 Find out the the molar volume of CO_2 at 500 K and 100 atm if it behaves as a van der Waals gas.

Solution We know,

$$\left(P + \frac{a}{V_m{}^2}\right)(V_m - b) = RT$$

or

$$V_m^2\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RTV_m^2$$

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or

$$\left(PV_m^2 + a\right)(V_m - b) = RTV_m^2$$

or

$$PV_m^3 + aV_m - PbV_m^2 - ab = RTV_m^2$$

or

$$PV_m^3 - (Pb + RT)V_m^2 + aV_m = ab$$

or

$$V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0$$

For CO_2, $a = 3.61$ atm L^2 mol^{-2}, $b = 4.29 \times 10^{-2}$ L mol^{-1}. Now,

$$b + \frac{RT}{P} = 4.29\times10^{-2}\,\text{L mol}^{-1} + \frac{0.082\,\text{L atm K}^{-1}\text{mol}^{-1} \times 500\,\text{K}}{100\,\text{atm}}$$

$$= 0.453\,\text{L mol}^{-1}$$

$$\frac{a}{P} = \frac{3.61\,\text{atm L}^2\text{mol}^{-2}}{100\,\text{atm}} = 0.0361\,\text{L}^2\text{mol}^{-2}$$

$$\frac{ab}{P} = \frac{3.61\,\text{atm L}^2\text{mol}^{-2} \times 4.29\times10^{-2}\,\text{L mol}^{-1}}{100\,\text{atm}} = 1.55\times10^{-3}\,\text{L}^3\,\text{mol}^{-3}$$

Considering

$$V_m = x, \quad x^3 - 0.453x^2 + 0.0361x - 1.55\times10^{-3} = 0$$

The acceptable value of $x = 0.366$. Therefore, the value of molar valume, $V_m = 0.366$ L mol^{-1}. ■

EXAMPLE 6.3 Define equation of state in terms of reduced variables for van der Waals gases.

Solution van dar Waals equation for 1 mol of a gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1}$$

we know,

$$P = P_R P_C, \quad V = V_R V_C, \quad T = T_R T_C \tag{2}$$

Therefore, equation (1) can be written as

$$\left[P_R P_C + \frac{a}{(V_R V_C)^2}\right](V_R V_C - b) = RT_R T_C$$

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Substituting critical values from example (6.1), we can write,

$$\left(\frac{P_R a}{27b^2} + \frac{a}{9V_R^2 b^2}\right)(3V_R b - b) = RT_R \frac{8a}{27Rb}$$

or

$$\frac{a}{27b^2}\left(P_R + \frac{3}{V_R^2}\right)b(3V_R - 1) = \frac{T_R 8a}{27b}$$

or

$$\left(P_R + \frac{3}{V_R^2}\right)(3V_R - 1) = 8T_R \tag{3}$$

Equation (3) is called *van der Waals reduced equation of state* which is applicable to all gases since it depends only on reduced values. This equation states that if two gases have same values of P_R and T_R, they will have same value of V_R. This is called *law of corresponding states.* ■

6.2 FUGACITY AND ACTIVITY

From Equation (5.160) of Chapter 5 we can write for 1 gm mol of a substance

$$\mu = \mu^\circ + \int_1^P \bar{V}\, dP \tag{6.7}$$

where μ and μ° are the molar free energies (chemical potentials) at P atm, and at 1 atm, respectively. If the system contains 1 gm mol of an ideal gas, then

$$\begin{aligned}\mu &= \mu^\circ + \int_1^P RT\, d \ln P \\ &= \mu^\circ + RT \ln P\end{aligned} \tag{6.8}$$

If the system changes from pressure P_1 to pressure P_2, the change in molar free energy can be written as

$$\mu_2 - \mu_1 = RT \ln \frac{P_2}{P_1} \tag{6.9}$$

But if the system contains a real gas, say, a van der Waals gas, for which

$$\bar{V} = \frac{RT}{P} + \left(b - \frac{a}{RT}\right)\frac{RT}{P\bar{V}} \tag{6.10}$$

If $P\bar{V} \approx RT$, equation (6.10) would approximate to

$$\bar{V} \approx \frac{RT}{P} + \left(b - \frac{a}{RT}\right) \tag{6.11}$$

Hence,

$$\mu = \mu^\circ + \int_1^P \left[\frac{RT}{P} + \left(b - \frac{a}{RT}\right)\right] dP \tag{6.12}$$

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Since $[b - a/(RT)] = B$, B being the second virial coefficient of the virial equation for gases (see Equation 6.1).

EXAMPLE 6.4 Transform the van der Waals equation into the virial equation and show that the second virial coefficient is $[b - a/(RT)]$, consider 1 gm mol of the gas.

Solution We have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

or

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = RT(V - b)^{-1} - \frac{a}{V^2} = \frac{RT}{V}\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$

or

$$PV = RT\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \frac{1}{2}\left(\frac{b}{V}\right)^2 + \cdots\right] \cong RT\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{V}\right]$$

Comparing with the virial equation

$$PV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \cdots\right)$$

we have $B = (b - \frac{a}{RT})$. We have from Equation (6.12),

$$\mu = \mu^\circ + RT \ln P + B(P - 1) \tag{6.13}$$

Hence the change in partial molar free energy in going from state 1 to state 2 can be written as

$$\mu_2 - \mu_1 = RT \ln \frac{P_2}{P_1} + B(P_2 - P_1) \tag{6.14}$$

Thus the third term on the right-hand side of Equation (6.13) is the correction term on account of non-ideality. It would also appear that the story of non-ideality is contained in the virial coefficient B.

Lewis introduced a new device to treat the problem of non-ideality. He expressed the chemical potential (molar free energy) μ of a real gas, by the equation

$$\mu = \mu^\circ + RT \ln f \tag{6.15}$$

Where f was termed as *fugacity* of the gas. Comparison of Equations (6.8) and (6.15), which have the same form, reveals that for an ideal gas fugacity is exactly equal to the pressure but for a non-ideal gas fugacity will be a property similar to, but not equal to, the pressure. The story of non-ideality is contained in the fugacity term.

In dealing with real gases, the standard state has to be defined as the state of unit fugacity, $f = 1$, a property which may be called the *true ideal pressure of a*

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real gas. Now, the change in molar free energy for the change of the system from state 1 to state 2 can be written as

$$\mu_2 - \mu_1 = RT \ln \frac{f_2}{f_1} \tag{6.16}$$

where f_1 and f_2 respectively are the fugacities of the gas under the observed pressures P_1 and P_2. It is known that at very low pressures the real gases tend to ideal behaviour. That is as $P \to 0$, $(f/P) = 1$. At higher pressures, however,

$$\frac{f}{P} = \gamma \text{ (say)} \quad \text{or} \quad f = \gamma P \tag{6.17}$$

where γ is called the *fugacity coefficient*; of course, γ depends on the pressure. In view of Equation (6.17) the relation (6.15) can be written as

$$\mu = \mu^\circ + RT \ln (\gamma P) = \mu^\circ + RT \ln P + RT \ln \gamma \tag{6.18}$$

A relationship between fugacity and the pressure of a real gas can be deduced as follows:

From Equation (6.11) it follows that the difference between the molar volumes of the ideal gas and the real gas can be written as

$$\bar{V}_{\text{real}} - \bar{V}_{\text{ideal}} = b - \frac{a}{RT} = B \tag{6.19}$$

Hence

$$\mu_2 - \mu_1 = \int_1^2 \bar{V}_{\text{real}}\, dP = \int_1^2 \left(\bar{V}_{\text{ideal}} + B\right) dP \tag{6.20}$$

In view of Equation (6.16) for real gas, the Equation (6.20) can be transformed into

$$\mu_2 - \mu_1 = RT \ln \frac{f_2}{f_1} = \int_1^2 \left(\frac{RT}{P} + B\right) dP$$

$$= RT \ln \frac{P_2}{P_1} + \int_1^2 B\, dP \tag{6.21}$$

Therefore,

$$RT \ln \frac{P_1 f_2}{f_1} = RT \ln P_2 + \int_1^2 B\, dP \tag{6.22}$$

At low pressures as $P \to 0$, $f_1 = P_1$ (at low pressures) and at any higher pressure P, $f_2 = f$. Hence

$$RT \ln f = RT \ln P + \int_0^P B\, dP$$

or

$$RT \ln f = RT \ln P + BP \tag{6.23}$$

or

$$f = P \exp \frac{BP}{RT} \tag{6.24}$$

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From Equation (6.24), expression for fugacity coefficient γ can be easily deduced using the relationship (6.17), i.e.

$$\gamma = \exp\frac{BP}{RT}$$

EXAMPLE 6.5 A gas obeys the equation of state $P(V - b) = RT$. For this gas $b = 0.0391$ dm^3 mol^{-1}. Calculate fugacity and the fugacity coefficient for the gas at 1000°C and 1000 atm.

Solution We know,

$$d\mu_{(\text{ideal})} = V_{m(\text{ideal})}\, dP \tag{1}$$

and

$$d\mu_{(\text{real})} = V_{m(\text{real})}\, dP \tag{2}$$

From equation (1),

$$\mu_{2(\text{ideal})} - \mu_{1(\text{ideal})} = \int_{P_1}^{P_2} V_{m(\text{ideal})} dP = RT \ln \frac{P_2}{P_1}$$

From equation (2)

$$\mu_{2(\text{real})} - \mu_{1(\text{real})} = \int_{P_1}^{P_2} V_{m(\text{real})}\, dP$$

For real gas,

$$\mu_{2(\text{real})} = \mu^{\circ}_{(\text{real})} + RT \ln f_2$$

and

$$\mu_{1(\text{real})} = \mu^{\circ}_{(\text{real})} + RT \ln f_1$$

Therefore,

$$\mu_{2(\text{real})} - \mu_{1(\text{real})} = RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} V_{m(\text{real})}\, dP$$

or

$$RT \ln \frac{f_2}{f_1} - RT \ln \frac{P_2}{P_1} = \int_{P_1}^{P_2} V_{m(\text{real})}\, dP - \int_{P_1}^{P_2} V_{m(\text{ideal})}\, dP$$

or

$$RT \ln \frac{f_2}{P_2} - RT \ln \frac{f_1}{P_1} = \int_{P_1}^{P_2} \left[V_{m(\text{real})} - V_{m(\text{ideal})}\right] dP \tag{3}$$

If pressure P_1 is very low so that the gas behaves ideally then

$$\lim_{P_1 \to 0} \frac{f_1}{P_1} = 1$$

and if $f_2 = f$ and $P_2 = P$ then equation (3) can be written as

$$RT \ln \frac{f}{P} = \int_0^P \left[V_{m(\text{real})} - V_{m(\text{ideal})}\right] dP$$

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Now in the present example

$$V_{(\text{real})} = \frac{RT}{P} + b = \frac{RT}{P} + 0.0391\,\text{dm}^3\,\text{mol}^{-1} \quad \text{and} \quad V_{(\text{ideal})} = \frac{RT}{P}$$

Therefore,

$$RT \ln\frac{f}{P} + \int_0^P (0.0391\,\text{dm}^3\text{mol}^{-1})\,dP = 0.0391\,\text{dm}^3\text{mol}^{-1}\left[P\right]_0^{1000}\text{atm}$$

$$= 0.0391\,\text{dm}^3\text{mol}^{-1} \times 1000\,\text{atm}$$

$$= 39.1\,\text{dm}^3\text{mol}^{-1}\text{atm}$$

or

$$\ln\frac{f}{P} = \frac{39.1\,\text{dm}^3\text{mol}^{-1}\text{atm}}{0.082\,\text{dm}^3\text{atm K}^{-1}\text{mol}^{-1} \times 1273\,\text{K}} = 0.375$$

or

$$\frac{f}{P} = 1.455 = \gamma = \text{Fugacity coefficient}$$

Hence

$f = 1.455 \times 1000$ atm $= 1455$ atm. ■

EXAMPLE 6.6 Starting with Equation (6.24) and assuming that molar volumes of the ideal and real gases are equal but not the pressures, show that the true pressure is the geometric mean of the fugacity and the ideal pressure.

Solution we know,

$$f = P\exp\frac{BP}{RT}$$

neglecting the second and higher powers in the expansion, we get

$$\frac{f}{P} \cong \left(1 + \frac{BP}{RT}\right)$$

Since $B = \overline{V}_{\text{real}} - \overline{V}_{\text{ideal}}$, we can write

$$\frac{f}{P} = 1 + \frac{P\overline{V}_{\text{real}}}{RT} - \frac{P\overline{V}_{\text{ideal}}}{RT}$$

Also, since $P\overline{V}_{\text{ideal}} = RT$, we write

$$\frac{f}{P} = \frac{P\overline{V}_{\text{real}}}{RT} - \frac{P\overline{V}_{\text{real}}}{P_{\text{ideal}}\overline{V}_{\text{ideal}}}$$

By assumption $\overline{V}_{\text{real}} = \overline{V}_{\text{ideal}}$, we obtain

$$\frac{f}{P} = \frac{P}{P_{\text{ideal}}} \quad \text{or} \quad P = \left(fP_{\text{ideal}}\right)^{1/2} \quad ■$$

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6.2.1 Fugacity from Compressibility Factor

For an ideal gas the compressibility factor is unity and hence

$$\overline{V}_{\text{ideal}} = \frac{RT}{P} \tag{6.25}$$

For a real gas, however,

$$\overline{V}_{\text{real}} = Z\frac{RT}{P} \tag{6.26}$$

From Equation (6.22) it follows that

$$RT \ln \frac{f}{P} = \int_0^P B\, dP$$

or

$$\ln \frac{f}{P} = \int_0^P \frac{1}{RT}\left(\overline{V}_{\text{real}} - \overline{V}_{\text{ideal}}\right) dP$$

or

$$\frac{f}{P} = \exp\left[\int_0^P \frac{1}{RT}\left(\overline{V}_{\text{real}} - \overline{V}_{\text{ideal}}\right)\right] dP \tag{6.27}$$

In view of Equations (6.25) and (6.26), Equation (6.27) can be transformed into

$$f = P\exp\left(\int_0^P \frac{Z-1}{P}\, dP\right) \tag{6.28}$$

The compressibility factor charts are available for gases. Hence the integral in Equation (6.28) can be evaluated and the value of the fugacity f can be calculated.

6.2.2 Standard States

All the effects of non-ideality of the gas are included in the fugacity coefficient γ (Equation 6.17). When the gas is ideal $\gamma = 1$. Deviations from ideality are measured by deviation of γ from unity.

The definition of the standard state is subtle and curious, since it is not any real state of the gas; it is an imaginary or a hypothetical state. We want to make the gas behave ideally in its standard state, so that we may compare properties of different gases in ideal standard states with one another and with theoretical calculations. In the standard state, all attractive and repulsive intermolecular forces are made to disappear. The advantage of the standard state, hypothetical albeit, is that it requires all gases to be in the same ideal condition when they are in their standard states.

But a question may be asked, how can we find the properties of a gas in an imaginary state? The determination is easy and can be understood from Figure 6.3.

At sufficiently low pressure, every gas approaches ideal behaviour and its fugacity equals its pressure. To get the property of a gas in its standard, we must

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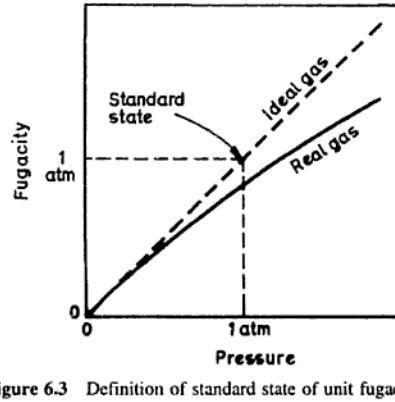

Figure 6.3 Definition of standard state of unit fugacity.

move along the experimental curve, as a function of pressure, until it joins the ideal curve, and then move back along the ideal curve until we reach the point of unit fugacity. Since we have simple equations for the properties of an ideal gas, there is no problem in calculating the change in a property along the ideal curve.

According to the law of corresponding states different gases display nearly the same deviations from ideality when they are in the corresponding states. This rule is illustrated by the fact that different gases have almost the same fugacity coefficients γ when they are at the same reduced temperature ($T_R = T/T_C$) and pressure ($P_R = P/P_C$). Figure 6.4 shows a family of curves relating the fugacity coefficient of a gas to P_R at various values of T_R. To the approximation that the law of corresponding states is valid all gases have the same value of γ when they are in the corresponding state. This is a useful principle, for it allows us to estimate the fugacity of a gas solely from a knowledge of its critical constants.

6.2.3 Use of Fugacity in Equilibrium Calculations

Let us consider the following reaction between non-ideal gases:

$$aA + bB \rightleftharpoons cC + dD$$

Here the small letters represent the stroichiometic numbers and the capital letters represent the reactants and product species. If the reactants and the products were non-ideal gases, we could write for the equilibrium constant

$$K_f = \frac{f_C^c f_D^d}{f_A^a f_B^b} \tag{6.29}$$

Equation (6.29), in view of Equation (6.17), can be transformed into

$$K_f = \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \frac{P_C^c P_D^d}{P_A^a P_B^b} = K_\gamma K_P \tag{6.30}$$

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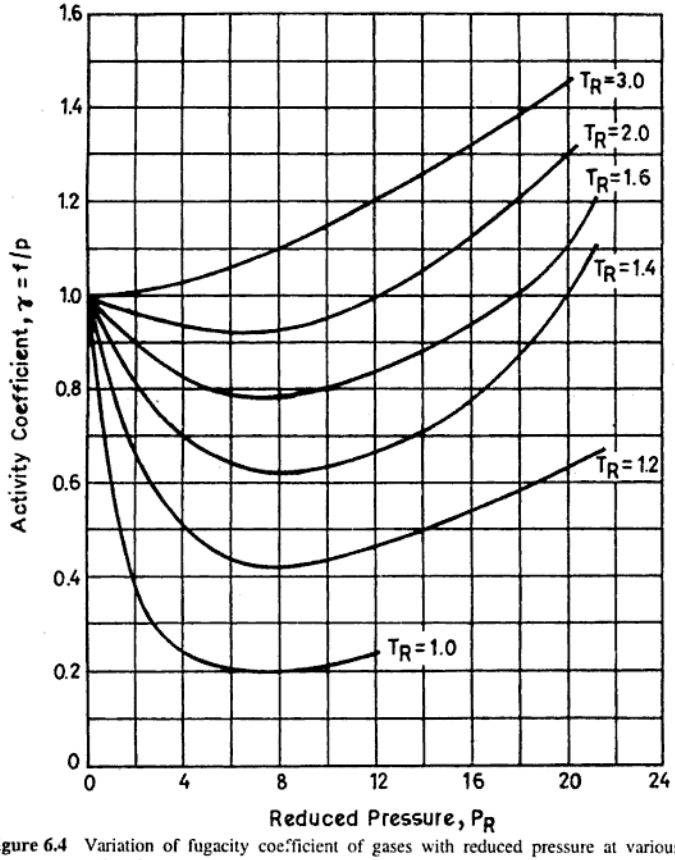

Figure 6.4 Variation of fugacity coefficient of gases with reduced pressure at various reduced temperatures. [R.H. Newton, *Ind. Eng. Chem.* 27 (1935) 302].

Of course, K_γ is not an equilibrium constant but simply the ratio of fugacity coefficients needed to convert the partial pressures in K_P into the fugacities in K_f.

6.3 ACTIVITY

The fugacity function is related to chemical potential through Equation (6.15) and in principle we could use fugacities to discuss equilibrium in liquid and solid solutions. In practice, however, a new function is introduced, the *activity*, a. The 'activity' is the ratio of fugacity to fugacity in a defined standard state,

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Now $c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ = \Delta_r G^\circ =$ standard reaction Gibbs energy. Therefore,

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} = \Delta_r G^\circ + RT \ln Q$$

Standard states for components in solution

To apply Equation (6.34) to practical problems, we must define standard states for components in the solution. There are two different standard states in common use, with increasing dilution, the solvent always approaches the ideal behaviour specified by Roult's law and the solute always approaches the behaviour specified by Henry's law. So there are two standard states — one based on Roult's law and the other based on Henry's law. Expression for Roult's law is discussed in Chapter 5 (Section 5.24.2). Henry's law can be understood as follows:

Consider a solution of component B which may be called the solute in A the solvent. If the solution is sufficiently diluted a condition ultimately is attained in which each molecule of B is effectively completely surrounded by component A. The solute B is then in a uniform environment irrespective of the fact that A and B may form solutions that are far from ideal at higher concentrations. In such a very dilute solution the escaping tendency of B from its uniform environment is proportional to its mole fraction (x_B) but, the proportionality constant k, unlike in Roult's law, is no longer P_B°, the vapour pressure of pure B. We may write

$$P_B = kx_B \tag{6.35}$$

Equation (6.35) is called *Henry's law*, named after its author, William Henry. Proportionality constant k is called Henry's law constant which is the characteristic of solute.

Now let us take up the definition of the standard states based on (i) Roult's law and on (ii) Henry's law.

Case I: Based on Roult's law. In this case, the standard state of component A considered as solvent, in a solution, is taken to be the pure liquid or pure solid at one atmosphere pressure and at the temperature in question. Thus the activity

$$a_A = \frac{f_A}{f_A^\circ} = \frac{P_A}{P_A^\circ} \tag{6.36}$$

where P_A° is the vapour pressure of pure A under one atmosphere total pressure. It is almost always sufficiently accurate to take the activity equal to the ratio of partial pressure P_A of A over the solution to the vapour pressure of pure A at one atmosphere pressure. It is always possible, however, to convert these vapour pressures to fugacities, should the vapour depart appreciably from ideal gas behaviour.

With this choice of standard state, Roult's law becomes

$$a_A = \frac{P_A}{P_A^\circ} = x_A \tag{6.37}$$

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6.4 DEVIATIONS FROM IDEALITY IN LIQUID SOLUTIONS

Difference between an ideal gas mixture and an ideal liquid solution is that in the former, forces of attraction and repulsion between the molecules are totally absent, whereas in the ideal liquid solution, the forces of attraction between solute–solute, solvent–solvent and solute-solvent are present, but all are identical. The ideal gas mixture obeys Dalton's law of partial pressure while the ideal liquid solutions obey Roult's law but the vapours obey Dalton's law. Volume change and enthalpy change on mixing for both ideal gas mixtures and ideal liquid solutions are zero.

In the liquid solutions if the interactions between unlike molecules are different from the interactions between the like molecules, it is said to be non-ideal solutions. In case of non-ideal liquid solutions, the volume and enthalpy changes on mixing are non-zero. The non-ideal solutions are classified depending upon whether they show a positive deviation from ideality or a negative deviation from ideality. If the interaction between the unlike molecules is stronger than the interaction between the like molecules, i.e. solute–solute or solvent–solvent, the tendency of each of the components to escape into the vapour phase is reduced and the system shows negative deviation from Roult's law, i.e.

$$f_i < x_i f_i^* \quad \text{or} \quad p_i < p_i^* x_i$$

the superscript* denotes that the quantity is for pure species ($x_i = 1$). This implies that the observed vapour pressure for mixtures showing negative deviations from ideality will be less than that predicted by Roult's law. A plot for acetone–chloroform system showing negative deviation is given in Figure 6.5, as an example. Some of the other systems showing negative deviations from Roult's law are chloroform–benzene, chloroform–dimethyl ether systems, etc. One of the factors responsible for the negative deviation is the predominance of specific

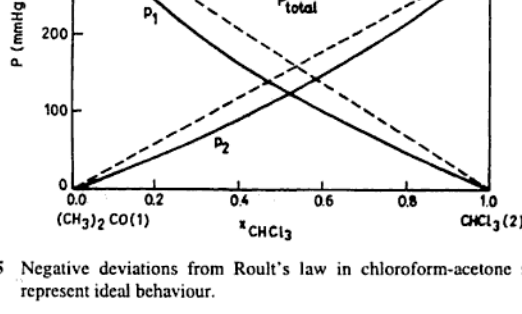

Figure 6.5 Negative deviations from Roult's law in chloroform-acetone system lines represent ideal behaviour.

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Enthalpy of mixing in a non-ideal solution is not equal to zero. Instead, we can derive as follows:

$$\begin{aligned}\Delta H_{\text{mixing}} &= \Delta G_{\text{mixing}} + T\Delta S_{\text{mixing}} \\ &= RT\sum n_i \ln a_i - RT^2 \sum n_i \left(\frac{\partial \ln a_i}{\partial T}\right)_P - RT\sum n_i \ln a_i \\ &= -RT^2 \sum n_i \left(\frac{\partial \ln a_i}{\partial T}\right)_P \qquad (6.48) \\ &= -RT^2 \sum n_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P \qquad \left[\text{as } \left(\frac{\partial \ln x_i}{\partial T}\right)_P = 0\right]\end{aligned}$$

Volume of ΔV_{mixing} for a non-ideal solution can be written

$$\begin{aligned}\Delta V_{\text{mixing}} &= \left(\frac{\partial \Delta G_{\text{mixing}}}{\partial P}\right)_T \\ &= RT\sum n_i \left(\frac{\partial \ln a_i}{\partial P}\right)_T \\ &= RT\sum n_i \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T \qquad \left[\text{as } \left(\frac{\partial \ln x_i}{\partial P}\right)_T = 0\right] \qquad (6.49)\end{aligned}$$

EXAMPLE 6.11 Acetone and chloroform are mixed to prepare 1 kg of a solution in which the mole fraction of chloroform (x_1) is 0.5. The partial molar volume of chloroform (V_1, m) is 80.235 $cm^3\ mol^{-1}$ and that of acetone ($V_{2,m}$) is 74.166 $cm^3\ mol^{-1}$. Calculate the volume of the solution.

Solution The total volume of solution is

$$V = n_1 V_{1,m} + n_2 V_{2,m}$$

Now

$$n_1 = \frac{n_1(n_1+n_2)}{n_1+n_2} = x_1(n_1+n_2) = \frac{w_1}{M_1}$$

$$n_2 = \frac{n_2(n_1+n_2)}{n_1+n_2} = x_2(n_1+n_2) = \frac{w_2}{M_2}$$

Then

$$V = x_1(n_1+n_2)V_{1,m} + x_2(n_1+n_2)V_{2,m} = (n_1+n_2)(x_1V_{1,m} + x_2V_{2,m})$$

Therefore,

$$w_1 + w_2 = x_1M_1(n_1+n_2) + x_2M_2(n_1+n_2) = (x_1M_1 + x_2M_2)(n_1+n_2)$$

and

$$n_1 + n_2 = \frac{w_1+w_2}{x_1M_1 + x_2M_2} = 11.5149$$

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Therefore $$V = \frac{w_1 + w_2}{x_1 M_1 + x_2 M_2}(x_1 V_{1,m} + x_2 V_{2,m}) \quad (1)$$

Given, $w_1 + w_2 = 1\,\text{kg} = 1000\,\text{g}$; $x_1 = 0.5$, $x_2 = 0.5$, $V_{1,m} = 80.235\ \text{cm}^3\text{mol}^{-1}$ $V_{2,m} = 74.166\ \text{cm}^3\text{mol}^{-1}$, $M_1 = 119.59\ \text{mol}^{-1}$, $M_2 = 58.0\ \text{g mol}^{-1}$. Substituting these values in equation (1), we get

$$V = \frac{1000(0.5 \times 80.235 + 0.5 \times 74.166)}{0.5 \times 119.59 + 0.5 \times 58.0} = 869.9\ \text{cm}^3 \quad \blacksquare$$

6.6 EXCESS FUNCTIONS

Deviations from ideal behaviour can best be expressed in terms of excess thermodynamic functions, which give a better quantitative idea about the nature of molecular interactions. The excess functions are also of much utility in the development of statistical theories based on fluid models.

The difference between the thermodynamic functions of mixing for a real system and the corresponding value for the ideal system at the same temperature and pressure is called the *excess thermodynamic function*. This quantity represents the excess (positive or negative) of a given thermodynamic property of the solution over the ideal (reference) solution. Denoting the excess functions by the superscript E, we can write

$$y^E = \Delta y_{(\text{mixture-real})} - \Delta y_{(\text{mixture-ideal})} \quad (6.50)$$

where y denotes any of the thermodynamic functions. With this definition, we can define expressions for different excess thermodynamic functions as follows:

(a) Excess chemical potential, μ^E

$$\begin{aligned} \mu_i^E &= \mu_{\text{real}} - \mu_{\text{ideal}} \\ &= (\mu_i^\circ + RT \ln x_i + RT \ln \gamma_i) - (\mu_i^\circ + RT \ln x_i) \\ &= RT \ln \gamma_i \end{aligned} \quad (6.51)$$

The standard state of the component in the ideal and in the non-ideal state have been taken to be the same, i.e.

$$\mu^\circ_{i\,(\text{ideal})} = \mu^\circ_{i\,(\text{real})}$$

(b) Excess Gibbs free energy, G^E

$$\begin{aligned} G^E &= \Delta G_{(\text{mixture-real})} - \Delta G_{(\text{mixture-ideal})} \quad (6.52) \\ &= RT \sum n_i \ln a_i - RT \sum n_i \ln x_i \\ &= RT \left(\sum n_i \ln x_i + \sum n_i \ln \gamma_i - \sum n_i \ln x_i \right) \\ &= RT \sum n_i \ln \gamma_i \quad (6.53) \end{aligned}$$

and for a binary mixture,

$$G^E = RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2)$$

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Solution For equimolar mixture, $x_1 = x_2 = 0.5$, Therefore,

$V^E/\text{cm}^3\,\text{mol}^{-1} = 0.5 \times 0.5\,[0.585 + 0.085(0.5 - 0.5) - 0.165(0.5 - 0.5)^2] = 0.146$ ■

6.7 GIBBS–DUHEM–MARGULES EQUATION

This equation provides information concerning the partial vapour pressure and the composition of various components in a solution. Starting with the Gibbs–Duhem equation (see Section 5.2), which for a binary solution can be written as

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{6.57}$$

at constant temperature and pressure. Dividing Equation (6.57) by the total number of moles, i.e. $(n_1 + n_2)$ we can write

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{6.58}$$

Now writing $\mu_i = \mu_i(T, P, x_i)$, we can write

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,x_i} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P} dx_i$$

which, at constant temperature and pressure, reduces to

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P} dx_i \tag{6.59}$$

Equation (6.59), in view of Equation (6.58), can be further transformed into

$$x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} dx_2 = 0 \tag{6.60}$$

Expressing chemical potential μ_i in terms of fugacity f_i for non-ideal solution as, $\mu_i = \mu_i^\circ + RT \ln f_i$, we can write from Equation (6.60)

$$RT\left[x_1 \left(\frac{\partial \ln f_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \ln f_2}{\partial x_2}\right)_{T,P} dx_2\right] = 0 \tag{6.61}$$

Since $x_1 + x_2 = 1$ and $dx_1 = -dx_2$, we get from Equation (6.61)

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1}\right)_{T,P} - x_2 \left(\frac{\partial \ln f_2}{\partial x_2}\right)_{T,P} = 0$$

or

$$\frac{d \ln f_1}{dx_1/x_1} - \frac{d \ln f_2}{dx_2/x_2} = 0$$

or

$$\frac{d \ln f_1}{d \ln x_1} - \frac{d \ln f_2}{d \ln x_2} = 0 \tag{6.62}$$

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We have from Equations (6.66) and (6.67)

$$\frac{dP}{dx_1} = \frac{dp_1}{dx_1}\left(1 - \frac{x_1 y_2}{x_2 y_1}\right) \tag{6.68}$$

Equation (6.68) gives the change in total pressure with the change in composition and is useful in the discussion of fractional distillation process.

Now if the addition of component 1 to the mixture increases the total vapour pressure then dP/dx_1 is positive and the right-hand side of Equation (6.68) will also be positive. Since dp_1/dx_1 is always positive for such a case,

$$1 - \frac{x_1 y_2}{x_2 y_1}$$

should also be positive, i.e.

$$\frac{x_1 y_2}{x_2 y_1} < 1$$

or

$$\frac{x_1(1-y_1)}{(1-x_1)y_1} < 1$$

Therefore,

$$x_1 < y_1 \quad \text{or} \quad y_1 > x_1 \tag{6.69}$$

This is Konovalov's first law which may be stated as follows: A saturated vapour in equilibrium with a binary liquid mixture is richer in that component whose addition to the liquid mixture, at constant temperature increases the total vapour pressure. This also implies that the vapour phase is richer in the component, which is more volatile.

Equaiton (6.68) can also be used to study the relation between the compositions of the vapour phase and the liquid phase for mixtures showing positive and negative deviations from Roult's law, i.e. those mixtures which show a maxima or a minima in the vapour pressure–composition diagram. The solutions with minimum or maximum boiling points are called *azeotropes*. Azeotropic solutions have identical compositions in liquid and vapour phases.

At maxima or minima,

$$\frac{dP}{dx_1} = 0$$

Hence from Equation (6.68) it follows that

$$\frac{dP}{dx_1} = 0 = \frac{dp_1}{dx_1}\left(1 - \frac{x_1 y_2}{x_2 y_1}\right)$$

Since $dp_1/dx_1 \neq 0$, we have

$$1 - \frac{x_1 y_2}{x_2 y_1} = 0$$

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Therefore,

$$a_{\pm} = a^{1/\upsilon} = \left(m^2\gamma_{\pm}^2\right)^{1/2} = m\gamma_{\pm}$$

(ii) We have

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^-$$

From equation (1),

$$a = m^{\upsilon_+} m^{\upsilon_-} \upsilon_+^{\upsilon_+} \upsilon_-^{\upsilon_-} \gamma_{\pm}^{\upsilon}$$

For $Zn(NO_3)_2$, $\upsilon_+ = 1$, $\upsilon_- = 2$. Then

$$a = 4m^3\gamma_{\pm}^3$$

Therefore,

$$a_{\pm} = a^{1/\upsilon} = \left(4m^3\gamma_{\pm}^3\right)^{1/3} = (4)^{1/3} m\gamma_{\pm}$$

(iii) We have

$$Na_3PO_4 \rightarrow 3Na^+ + PO_4^{3-}, \quad \upsilon_+ = 3, \quad \upsilon_- = 1$$

From equation (1),

$$a = 27m^4\gamma_{\pm}^4$$

Therefore,

$$a_{\pm} = a^{1/\upsilon} = \left(27m^4\gamma_{\pm}^4\right)^{1/4} = (27)^{1/4} m\gamma_{\pm} \quad \blacksquare$$

EXAMPLE 6.14 **Find out (i) activity (a) of the following electrolytes in a solution at 25°C:**

(a) 0.01 m $ZnCl_2$ $(\gamma_{\pm} = 0.71)$

(b) 0.005 m $CuSO_4$ $(\gamma_{\pm} = 0.53)$

Also, find out (ii) mean ionic activity ($a_{\pm}$) and mean molality ($m_{\pm}$) of the above mentioned electrolytes in solution.

Solution (i) (a) 0.01 m $ZnCl_2$ ($\gamma_{\pm} = 0.71$). For $ZnCl_2$, $\upsilon_+ = 1$, $\upsilon_- = 2$, $\upsilon = \upsilon_+ + \upsilon_- = 3$. Then

$$a = m^{\upsilon}\upsilon_+^{\upsilon_+}\upsilon_-^{\upsilon_-}\gamma_{\pm}^{\upsilon} = (0.01)^3(2^3)(0.71)^3 = 1.43 \times 10^{-6}$$

(i) (b) 0.005 m $CuSO_4$ ($\gamma_{\pm} = 0.53$). For $CuSO_4$, $\upsilon_+ = 1$, $\upsilon_- = 1$, $\upsilon = \upsilon_+ + \upsilon_- = 2$. Then

$$a = m^{\upsilon}\upsilon_+^{\upsilon_+}\upsilon_-^{\upsilon_-}\gamma_{\pm}^{\upsilon} = (0.005)^2(0.53)^2 = 7.02 \times 10^{-6}$$

(ii) For 0.01 m $ZnCl_2$, $a_{\pm} = a^{1/\upsilon}$. Then

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$$
\begin{aligned}
m_{\pm} &= (m_+^{v+} m_-^{v-})^{1/v} \\
&= \left[(mv_+)^{v+}(mv_-)^{v-}\right]^{1/v} \\
&= (m^v v_+^{v+} v_-^{v-})^{1/v} \\
&= m(v_+^{v+} v_-^{v-})^{1/v} \\
&= 0.01(2^2)^{1/3} \\
&= 1.59 \times 10^{-2}
\end{aligned}
$$

For 0.005 m $CuSO_4$,

$a_{\pm} = a^{1/v}$. Then $m_{\pm} = 0.005(1)^{1/2} = 0.005$ ■

6.9.1 Activity Coefficients from Freezing Point Depression

If T_0 is the freezing point of the pure solvent and T_f is the freezing point of the solution then $T_0 - T_f = \Delta T_f$ is the *depression* of freezing point.

Let us consider the freezing of the pure liquid solvent 1. At the freezing point, the solid and liquid phases are in equilibrium. This can be expressed by saying that the chemical potentials of the solvent 1 in the two phases are equal. But as the non-volatile solutes added to the liquid phase, the escaping tendency of the solvent molecules from liquid to solid decreases whereas the reverse escaping tendency, i.e. from solid to liquid is unaffected. The crystal of the solvent begin to dissolve. To prevent this and to restore equilibrium, we must favour the solid phase by lowering the temperature. At some lower temperature, the two escaping tendencies again match and the equilibrium is established.

The requirement of the equality of chemical potential of the solvent 1 in the two phases yields

$$\mu_1^s = \mu_1^l = \mu_1^{ol} + RT \ln x_1^l \tag{6.78}$$

where μ_1^{ol} is the chemical potential of pure liquid 1 and x_1^l is its mole fraction in solution.

As the solute is added, $\ln x_1^l$ term falls. As the temperature T is lowered in compensation, both μ_1^s and μ_1^{ol} rise. But μ_1^{ol} rises faster than μ_1^s because the molar entropy of the liquid is greater than that of solid and the ordering effect of the temperature drop is more pronounced. At some lower temperature, the large rise in μ_1^{ol} and small drop in $m \ln x_1^l$ due to addition of solute balance the small rise in μ_1^s. So, Equation (6.78) is again balanced. Writing in the differential form, we have

$$d\mu_1^s = d\mu_1^l \tag{6.79}$$

In the present case,

$$\mu_1^s = f(T, P)$$

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or

$$d\mu_1^s = \left(\frac{\partial \mu_1^s}{\partial T}\right)_P dT + \left(\frac{\partial \mu_1^s}{\partial P}\right) dP \tag{6.80}$$

If pressure is held constant, we can write from Equation (6.80) that

$$d\mu_1^s = \bar{S}_1^s \, dT \tag{6.81}$$

where $\bar{S}_1^s$ is the molar entropy of 1 in the solid phase. Similarly, for the liquid phase

$$\mu_1^l = f(T, P, x_1)$$

or

$$d\mu_1^l = \left(\frac{\partial \mu_1^l}{\partial T}\right)_{P,x_1} dT + \left(\frac{\partial \mu_1^l}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{T,P} dx_1 \tag{6.82}$$

If pressure is held constant, it follows from Equation (6.82) that

$$d\mu_1^l = -\bar{S}_1^l dT + RT\, d \ln x_1^l \tag{6.83}$$

where $\bar{S}_1^l$ is the molar entropy of 1 in the liquid phase. From Equations (6.79), (6.81) and (6.83), we can write

$$(\bar{S}_1^l - \bar{S}_1^s)\, dT = RT d \ln x_1^l$$

or

$$d \ln x_1^l = \frac{\Delta H_{\text{fusion}}}{RT^2} dT \tag{6.84}$$

If the molar heat of fusion ΔH_{fusion} is taken to be constant, integration of Equation (6.84) between the limits, when $x_1^l = 1$, $T = T_0$ and $x_1^l = x_1$, $T = T_f$, then yields

$$\int_1^{x_1} d \ln x_1^l = \frac{\Delta H_{\text{fusion}}}{R} \int_{T_0}^{T_f} \frac{dT}{T^2}$$

or

$$\ln x_1 = -\frac{\Delta H_{\text{fusion}}}{R}\left(\frac{1}{T_f} - \frac{1}{T_0}\right)$$

$$\ln x_1^l \cong -\frac{\Delta H_{\text{fusion}}}{RT_0^2} \Delta T_f \quad (\text{considering } T_f T_0 \approx T_0^2) \tag{6.85}$$

Equation (6.85) gives the relationship from which molecular weights can be calculated from the freezing point depression data.

Writing $\ln x_1$ as $\ln (1 - x_2)$ and expanding it in the power series of the mole fraction of solute x_2, we get

$$\ln x_1 = \ln (1 - x_2) = -x_2 - \frac{1}{2} x_2^2 - \cdots \tag{6.86}$$

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Neglecting the square and higher power terms in the expansion, because the solution is very dilute, we get from Equation (6.85)

$$x_2 \cong \frac{\Delta H_{\text{fusion}}}{RT_0^2}\Delta T_f \tag{6.87}$$

or

$$\Delta T_f = \frac{RT_0^2}{\Delta H_{\text{fusion}}} x_2$$

For dilute solution,

$$x_2 = \frac{n_2}{n_1} \tag{6.88}$$

where m is the molality of the solution and M_1 is the molecular weight of the solvent. Then

$$\Delta T_f = \frac{RT_0^2}{\Delta H_{\text{fusion}}}\frac{n_2}{n_1}$$

Now

$$m = \frac{n_2}{n_1 M_1}$$

Therefore,

$$\frac{n_2}{n_1} = mM_1 \tag{6.89}$$

and

$$\Delta T_f = K_f m,$$

where

$$K_f = \frac{RT_0^2 M_1}{\Delta H_{\text{fusion}}} \tag{6.90}$$

and is called the *molal freezing point depression constant* or *the cryoscopic constant* of the solvent.

EXAMPLE 6.15 When 3.0 g of sucrose is dissolved in 100 g of water, the solution freezes at −0.16 K. Calculate the molecular weight of sucrose. Given that, the cryoscopic constant of water is 1.86 K kg mol^{-1}.

Solution We know, $\Delta T_f = K_f m$. Then

$$\Delta T_f = T_0 - T_f = 0\,\text{K} - (-0.16\,\text{K}) = 0.16\,\text{K}$$

Therefore,

$$0.16\,\text{K} = 1.86\,\text{K kg mol}^{-1}\,\frac{(3/M_2)\,\text{mol}}{100 \times 10^{-3}\,\text{kg}}$$

where M_2 = Molecular weight of sucrose. Then M_2 = 348.75. ■

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EXAMPLE 6.16 The freezing point of pure benzene is lowered by 0.088 K for a 0.45% solution of monoclinic sulphur in benzene. Find out the molecular formula of sulphur in benzene. The cryoscopic constant of benzene is 5.07 K kg mol^{-1} .

Solution We know $\Delta T_f = K_f m$. In 100 g solution, the amount of sulphur is 0.45 g and the amount of benzene is (100 – 0.45) g = 99.55 g. Then

$$0.088 \text{ K} = 5.07 \text{ K kg mol}^{-1} \frac{(0.45/M_s) \text{ mol}}{99.55 \times 10^{-3} \text{ kg}}$$

where M_s = molar mass of sulphur. We get, M_s = 260 g mol^{-1}. Atomic weight of sulphur is 32.06. Now, 260/32.06 = 8.1 ≈ 8. Therefore, molecular formula is S_8.

For a non-ideal dilute solution, we can write from Equation (6.84)

$$\frac{d \ln a_1}{dT} = \frac{\Delta H_{\text{fusion}}}{RT^2} \tag{6.91}$$

Since the freezing point depression $\Delta T = T_0 - T, T^2 \approx T_0^2$ and $d(\Delta T) = -dT$. Then

$$d \ln a_1 = -\frac{\Delta H_{\text{fusion}}}{RT_0^2} d(\Delta T) \tag{6.92}$$

In view of Gibbs–Duhem equation,

$$n_1 d \ln a_1 + n_2 d \ln a_2 = 0$$

it follows from Equation (6.92)

$$\frac{n_2}{n_1} d \ln a_2 = \frac{\Delta H_{\text{fusion}}}{RT_0^2} d(\Delta T)$$

or

$$d \ln a_2 = \frac{1}{m_2 K_f} d(\Delta T) \tag{6.93}$$

where m_2 is the number of moles of 2 in 1 kg of the solvent 1. From Equation (6.77), we have

$$a_2 = a_{\pm}^{\upsilon} = \gamma_{\pm}^{\upsilon} m^{\upsilon} (\upsilon_+^{\upsilon+} \upsilon_-^{\upsilon-})$$

So that

$$d \ln a_{\pm} = d \ln \gamma_{\pm} m = d \ln \gamma_{\pm} + d \ln m = \frac{d(\Delta T)}{\upsilon m K_f} \tag{6.94}$$

Let

$$j = 1 - \frac{\Delta T}{\upsilon m K_f}$$

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$$M_2 = \frac{1.35 \times 82 \times 300 \times 1013250}{100 \times 9.9 \times 980.67} = 34660 \text{ g mol}^{-1} \quad \blacksquare$$

EXAMPLE 6.18 Calculate the osmotic pressure of a solution of 2.6 g of protein dissolved in 250 mL of water at 25°C. Molar mass of protein is 85000 g mol^{-1}.

Solution We have osmotic pressure,

$$\Pi V = n_2 RT \quad \text{or} \quad \Pi = \frac{n_2}{V} RT$$

Then

$$\Pi = \frac{(2.6/85000) \text{ mol} \times 82 \text{ atm} \cdot \text{mL} \cdot \text{K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{250 \text{ mL}}$$
$$= 2.99 \times 10^{-3} \text{ atm} \quad \blacksquare$$

EXAMPLE 6.19 Find out the ebullioscopic constant (K_b) of water.

Solution Ebullioscopic constant of water,

$$K_b = \frac{RT_b^2 M_1}{\Delta_{vap} H}$$
$$= \frac{(8.314 \text{ JK}^{-1}\text{mol}^{-1})(373.15 \text{ K})^2 (18.015 \times 10^{-3} \text{ kg})}{40.7 \times 10^3 \text{ Jmol}^{-1}}$$
$$= 0.51 \text{ K kg mol}^{-1} \quad \blacksquare$$

6.9.2 Activity Coefficient from Solubility Data

This method is applied to sparingly soluble salts, e.g. AgCl. For a solution of AgCl in water, we have

$$\text{AgCl(s)} \rightleftharpoons \text{AgCl(aq)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

for which we can write the expression for solubility product K_{sp} as

$$K_{sp} = a_{Ag^+} a_{Cl^-} = a_+ a_- = \gamma_+ \gamma_- C_+ C_- \tag{6.98}$$

where C is the molar concentration. The solubility of AgCl is simply

$$C_S = C_+ = C_-$$

Therefore,

$$K_{sp} = \gamma_\pm^2 C_S^2$$

or

$$\gamma_\pm = \frac{\sqrt{K_{sp}}}{C_S} \tag{6.99}$$

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EXAMPLE 6.20 The solubility product of sparingly soluble salt CaF_2 is 4.0×10^{-11}. Find out the value of activity coefficient.

Solution At infinite dilution, the activity coefficient approaches 1 and therefore $a_+ = C_+ = C_S$.

The method is to plot the value of solubility of salt for a series of solutions containing decreasing concentration of added electrolyte, i.e. logarithm of solubility is plotted against the square root of ionic strength.

Next step is to find out solubility by extrapolating the line to $I = 0$. At this situation, $a_+ = C_S$. Now,

$$CaF_2(s) \rightleftharpoons CaF_2(aq) \rightleftharpoons Ca^{+2}(aq) + 2F^-(aq)$$

Then

$$K_{sp} = C_S(2C_S)^2 = 4C_S^3$$

Therefore,

$$C_S = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{4 \times 10^{-11}}{4}\right)^{1/3} = 4.64 \times 10^{-4}$$

But,

$$K_{sp} = a_{Ca^{+2}}\left(2a_{F^-}\right)^2 = 4a_{Ca^{+2}}\gamma_+ C_{F^-}\gamma_-^2$$

or

$$K_{sp} = 4C_S^2\gamma_\pm^3$$

Therefore,

$$\gamma_\pm = \left(\frac{K_{sp}}{4C_S^2}\right)^{1/3} = \left[\frac{4 \times 10^{-11}}{4 \times (4.64 \times 10^{-4})^2}\right]^{1/3} = 0.0167 \quad \blacksquare$$

Equation (6.99) can be utilized for the evaluation of activity coefficients.

6.9.3 Activity Coefficient from e.m.f. Measurements

Consider the chemical cell schematically represented as

$$(Pt)H_2(g)\left|HCl(m)\right|AgCl(s)\left|Ag(s)\right.$$

This is a chemical cell without a liquid junction. The electrode reactions are

$$\frac{1}{2}H_2(g) \rightleftharpoons H^+(aq) + e$$

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-(aq)$$

The overall cell reaction is

$$\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(aq) + Cl^-(aq)$$

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Equation for the e.m.f. of the cell is (see Chapter 5 Section 5.24.6)

$$E = E^\circ - \frac{RT}{F} \ln \frac{a_{Ag} a_{H^+} a_{Cl^-}}{a_{AgCl}\, a_{H_2}^{1/2}} \tag{6.100}$$

Setting the activities of solid phases equal to unity and choosing hydrogen pressure so that $a_{H2} = 1$ (for ideal gas $P = 1$ atm), we obtain the equation

$$\begin{aligned} E &= E^\circ - \frac{RT}{F} \ln a_{H^+} a_{Cl^-} \\ &= E^\circ - \frac{2RT}{F} \ln a_\pm \\ &= E^\circ - \frac{2RT}{F} \ln \gamma_\pm m \end{aligned} \tag{6.101}$$

Equation (6.101) can be utilized for determining the value of $\gamma_\pm$ for HCl from the e.m.f data. According to Debye–Hückel's theory (to be given in the next section) in dilute solution, $\ln \gamma_\pm = -Am^{1/2}$ when A is a constant. Hence Equation (6.101) becomes

$$E + \frac{2RT}{F} \ln m = E^\circ + \frac{2RTA}{F} m^{1/2} \tag{6.102}$$

If the quantity on the left is plotted against $m^{1/2}$ and extrapolated back to $m = 0$ the intercept at $m = 0$ gives the value of E°. Once the standard e.m.f is determined in this way, Equation (6.101) can be used to calculate the mean activity coefficient for HCl from the e.m.f data. Similar procedure can be adopted for other strong electrolytes by constructing suitable electro-chemical cells.

EXAMPLE 6.21 The e.m.f. of the cell

$$\mathrm{Zn(s)} \left| \begin{matrix} \mathrm{ZnCl_2(aq)} \\ m = 0.01 \end{matrix} \right| \mathrm{AgCl(s)} \left| \mathrm{Ag(s)} \right.$$

is 1.16 volt at 25°C. Find out the mean activity coefficient of $ZnCl_2$ solution. Given

$$E^\circ_{Zn^{+2}/Zn} = -0.76 \text{ V}; \qquad E^\circ_{Ag/AgCl/Cl^-} = 0.22 \text{ V}$$

Solution The electrode reactions are

$$\mathrm{Zn(s)} \rightleftharpoons \mathrm{Zn^{2+}(aq)} + 2e$$

$$\mathrm{2AgCl\,(s)} + 2e \rightleftharpoons \mathrm{2Ag\,(s)} + \mathrm{2Cl^-}$$

The overall cell reaction is

$$\mathrm{Zn\,(s)} + \mathrm{2AgCl(s)} \rightleftharpoons \mathrm{ZnCl_2(aq)} + \mathrm{2Ag(s)}$$

The e.m.f. of the cell is

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln \frac{a_{ZnCl_2} a_{Ag}^2}{a_{Zn} a_{AgCl}^2}$$

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or

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{2F} \ln a_{Zn^{+2}} a^2_{Cl^-} \quad (1)$$

Now

$$\begin{aligned} a_{Zn^{+2}} a^2_{Cl^-} &= m_+ \gamma_+ m^2_- \gamma^2_- \\ &= m_+ m^2_- \gamma_+ \gamma^2_- \\ &= m\nu_+ (m\nu_-)^2 \gamma^3_{\pm} \\ &= m(2m)^2 \gamma^3_{\pm} \\ &= 4m^3 \gamma^3_{\pm} \end{aligned}$$

Therefore, from equation (1),

$$1.16 \text{ V} = 0.98 \text{ V} - 29.59 \times 10^{-3} \text{ V} \log (4m^3 \gamma^3_{\pm})$$

Here,

$$E^{\circ}_{cell} = 0.22 \text{ V} - (-0.76) \text{ V} = 0.98 \text{ V}$$

$$0.18 \text{ V} = -29.59 \times 10^{-3} \text{ V} \log 4(0.01)^3 - 29.59 \times 10^{-3} \text{ V} \log \gamma^3_{\pm}$$

or

$$0.18 \text{ V} = 0.1597 \text{ V} - 0.089 \text{ V} \log \gamma_{\pm}$$

or

$$0.0203 \text{ V} = -0.089 \text{ V} \log \gamma_{\pm}$$

or

$$\gamma_{\pm} = 0.59$$

6.10 VARIATION OF ACTIVITY COEFFICIENTS WITH CONCENTRATION

It has been generally observed that quite typically the coefficients decline quite markedly with increase in concentration in dilute solutions but then pass through minima and rise again in more concentrated solutions. The interpretation of the behaviour consists one of the principal problems in the theory of strong electrolytes.

The effect of interionic forces is to decrease the chemical potential of the solute and hence to decrease γ. The effect of ions on the solvent molecules is to hold the solvent more tightly in solution thereby decreasing its vapour pressure or fugacity. This effect decreases the γ of the solvent and conversely, as can be seen from the Gibbs–Duhem relation, it increases the γ of the solute. We can see, therefore, in general way why the log γ versus molality curves pass through a minima. Actually, however, the effects in more concentrated solution are too complicated for any simple model.

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$$N_i' = N_i e^{-\varepsilon_p/(kT)}$$

If an ion of charge Q_i is brought to a region of potential U, its potential energy is Q_iU. For such ions, the Boltzmann equation is therefore

$$N_i' = N_i e^{-Q_iU/(kT)} \tag{6.104}$$

The charge density in a region whose potential (U) is simply the summation of this expression over the different kinds of ion that may be present in the solution, each multiplied by its appropriate charge Q_i.

$$\sigma = \sum N_i'Q_i = \sum N_iQ_ie^{-Q_iU/(kT)} \tag{6.105}$$

The Debye–Hückel treatment now considers a solution so dilute that ions will rarely be close together. This condition implies that the interionic potential energy is small, and indeed much less than the average thermal energy, so that $Q_iU \ll kT$. Then the exponential factor in Equation (6.104) may be expanded as follows:

$$e^{-Q_iU/(kT)} = 1 - \frac{Q_iU}{kT} + \frac{1}{2!}\left(\frac{Q_iU}{kT}\right)^2 - \cdots$$

Terms higher than the second being negligible, Equation (6.105) becomes

$$\sigma = \sum N_iQ_i - \frac{U}{kT}\sum N_iQ_i^2$$

The first term vanishes by virtue of the requirement of overall electrical neutrality, and with $Q_i = z_ie$,

$$\sigma = -\frac{e^2U}{kT}\sum N_iz_i^2 \tag{6.106}$$

It should be noted that $\sum N_iz_i^2$ is closely related to the ionic strength, which is defined as $I = \frac{1}{2}\sum m_iz_i^2$. By substituting Equation (6.106) into Equation (6.103), there is obtained the Poisson–Boltzmann equation,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dU}{dr}\right) = \frac{4\pi e^2U}{\varepsilon kT}\sum N_iz_i^2$$

or,

$$\frac{d}{dr}\left(r^2\frac{dU}{dr}\right) = b^2r^2U \tag{6.107}$$

where,

$$b^2 = \frac{4\pi e^2}{\varepsilon kT}\sum N_iz_i^2 \tag{6.108}$$

The quantity $1/b$ has the dimensions of a length, and is called the *Debye length*. It may be thought of as an approximate measure of the thickness of the ionic atmosphere, i.e. the distance over which the electrostatic field of an ion extends with appreciable strength. For example, in a one-molar aqueous solution of uniunivalent electrolyte at 25°C, $1/b$ = 3.1Å.

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The Poisson–Boltzmann Equation (6.107) can be readily solved by making the substitution $u = rU$, whence $d^2u/dr^2 = b^2u$, so that

$$u = Ae^{-br} + Be^{br} \tag{6.109}$$

or

$$U = \frac{A}{r}e^{-br} + \frac{B}{r}e^{br}$$

A and B are constants in integration, to be determined from the boundary conditions. In the first place, U must vanish as r goes to infinity, so that

$$\frac{Ae^{-\infty}}{\infty} + \frac{Be^{\infty}}{\infty} = 0$$

This can be true only if $B = 0$, since the limit of e^r/r as r goes to infinity is not zero. We then have left,

$$U = \frac{A}{r}e^{-br}$$

The constant A can be determined by the fact that when $b = 0$, the concentration is zero, and therefore the potential is simply that of a single ion in the absence of any other charges, namely $U = ze/(\varepsilon r)$. Thus $ze/(\varepsilon r) = A/r$ and $A = ze/\varepsilon$. Therefore, the final solution becomes

$$U = \frac{ze}{\varepsilon r}e^{-br} \tag{6.110}$$

Once again, for the case of the very dilute solution (since b is a function of the concentration) the exponential may be expanded, giving

$$U = \frac{ze}{\varepsilon r}e^{-br} \approx \frac{ze}{\varepsilon r}(1 - br)$$

or

$$U \approx \frac{ze}{\varepsilon r} - \frac{zeb}{\varepsilon} \tag{6.111}$$

Here it is evident that the first term $ze/(\varepsilon r)$ is simply the potential at a distance r due to an ion of charge ze in a medium of dielectric constant ε. The term zeb/ε is then the potential due to the other ions, those forming the ionic atmosphere of the given ion. It is this extra potential that is related to the extra free energy of the ionic solution.

6.10.2 The Debye–Hückel Limiting Law

Let us imagine a given ion to be introduced into the solution in an uncharged state (this process requires negligible electrical energy). Then let us increase the charge Q gradually to its final value ze. The electrical energy required is

$$\Delta G = \int_0^{ze} U\,dQ = \int_0^{ze} \frac{-bQ}{\varepsilon}dQ = -\frac{b}{2\varepsilon}z^2e^2 \tag{6.112}$$

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Since $|\nu_+ z_+| = |\nu_- z_-|$,

$$\ln \gamma_\pm = -|z_+ z_-| \frac{e^2 b}{2\varepsilon kT} \tag{6.115}$$

The valence factor can be evaluated, as in Table 6.1, for the different electrolyte types:

Table 6.1 Valence factor

Type	Example	Ionic charges	Valence factor, $\lvert z_+ z_- \rvert$
Uniunivalent	KCl	$z_+ = 1, z_- = -1$	1
Unibivalent	$CaCl_2$	$z_+ = 2, z_- = -1$	2
Unitrivalent	$LaCl_3$	$z_+ = 3, z_- = -1$	3
Bibivalent	$ZnSO_4$	$z_+ = 2, z_- = -2$	4
Bitrivalent	$Fe_2(SO_4)_3$	$z_+ = 3, z_- = -2$	6

Let us now transform Equation (6.115) into base −10 logarithms and introduce the values of the universal constants. If e is taken as 4.80×10^{-10} esu, R must be 8.31×10^7 erg per °C per mole. The result is the Debye–Hückel limiting law for the activity coefficient,

$$\log \gamma_\pm = -1.825 \times 10^6 |z_+ z_-| \left(\frac{I\rho_0}{\varepsilon^3 T^3}\right)^{1/2} = -A|z_+ z_-| I^{1/2} \tag{6.116}$$

For water at 25°C, $\varepsilon = 78.54$, $\rho_0 = 0.997$, and Equation (6.116) becomes

$$\log \gamma_\pm = -0.509|z_+ z_-| I^{1/2} \tag{6.117}$$

In the derivation of the limiting law it was consistently assumed that the analysis applied only to dilute solutions. It is not to be expected therefore that the equation should hold for concentrated solutions, nor does it. As solutions become more and more dilute, however, the equation should represent the experimental data more and more closely. This expectation has been fulfilled by numerous measurements, so that the Debye–Hückel theory for very dilute solutions may be well substantiated.

In Figure 6.7, some experimental activity coefficients are plotted against the square roots of the ionic strengths. These data were obtained from the solubilities of sparingly soluble complex salts in the presence of added salts, such as NaCl, $BaCl_2$ and KNO_3. The straight lines indicate the theoretical curves predicted by the limiting law, and it is evident that these limiting slopes are followed at low ionic strengths. The Debye-Hückel theory gives correct quantitative results only at extreme dilutions. Note that the highest concentration in Figure 6.7 is about 0.01 M.

The theory can be improved by combining it with the general theory of non-ideal solutions. Thus the theory of the thermodynamic properties of strong electrolytes is now quite well understood. No simple theoretical equation for

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$$\text{Molality of } MgSO_4 = \frac{0.002 \text{ mol}}{100 \times 10^{-3} \text{ kg}} = 0.02 \text{ mol kg}^{-1}$$

Therefore, ionic strength,

$$I = \frac{1}{2}\sum m_i z_i^2$$

$$= \frac{1}{2}\left(m_{K^+}z_{K^+}^2 + m_{Cl^-}z_{Cl^-}^2 + m_{Mg^{+2}}z_{Mg^{+2}}^2 + 2m_{Cl^-}z_{Cl^-}^2 + m_{Mg^{+2}}z_{Mg^{+2}}^2 + m_{SO_4^{-2}}z^2{}_{SO_4^{-2}}\right)$$

$$= \frac{1}{2}\left(0.1 \times 1^2 + 0.1 \times 1^2 + 0.05 \times 2^2 + 2 \times 0.05 \times 1^2 + 0.02 \times 2^2 + 0.02 \times 2^2\right)$$

$$= 0.33 \text{ mol kg}^{-1} \quad \blacksquare$$

EXAMPLE 6.23 Calculate $\gamma_\pm$ in a 0.02 mol kg^{-1} HCl solution in CH_3OH at 25°C and 1 atm. For CH_3OH at 25°C and 1 atm, the dielectric constant is 32.6 and the density is 0.787 gm cm^{-3}.

Solution We know,

$$\log \gamma_\pm = -1.825 \times 10^6 \, |z_+ z_-| \left(\frac{I\rho_0}{\varepsilon^2 T^3}\right)^{1/2}$$

For CH_3OH at 25°C, $\varepsilon = 32.6$, $\rho = 0.787$ gm/cm^3. Ionic strength of HCl solution,

$$I = \frac{1}{2}(0.02 \times 1^2 + 0.02 \times 1^2) \text{ mol kg}^{-1}$$

$$= 0.02 \text{ mol kg}^{-1}$$

Therefore,

$$\log \gamma_\pm = -1.825 \times 10^6 \, |1 \times 1| \left[\frac{0.02 \times 0.787}{(32.6)^3 (298)^3}\right]^{1/2}$$

$$= -0.2393$$

or

$$\gamma_\pm = 0.58$$

QUESTIONS

1. What is the significance of equation of state written in terms of reduced variables?
2. What is the principle of law of corresponding states?
3. What is the difference between compressibility and compressibility factor?
4. The van der Waals equation of state takes into account:
   (a) Pressure correction only (b) Volume correction only (c) Both pressure and volume corrections (d) Neither of them. Choose the correct answer.

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17. In a solution of finite concentration of strong electrolytes, mean ionic activity coefficient is:
(a) Less than 1 (b) Greater than 1 (c) Equal to 1 (d) None of the above.
Choose the correct answer.

18. What are the dimensions of activity coefficient, chemical potential and fugacity?

19. The Debye–Hückel limiting law is applicable to:
(a) Dilute solution (b) Concentrated solution (c) Solution of weak electrolyte (d) None of the above.
Choose the correct answer.

20. The activity coefficients of strong electrolytes at high dilution should be determined in a given solvent and at a given temperature:
(a) Only by the ionic strength of the solution (b) Only by the valence type (z_+z_-) of the electrolyte (c) Both by the ionic strength of the solution and the valence type (z_+z_-) of the electrolyte (d) Not at all by the nature of the electrolyte.

21. A plot of $-\log \gamma_\pm$ versus $\sqrt{I}$ for all electrolytes should yield straight lines through:
(a) The value of $|z_+z_-|$ (b) The value of A (c) Zero (d) None of the above.
Choose the correct answer.

22. For a unitrivalent electrolyte the slope of the plot of $-\log \gamma_\pm$ versus $\sqrt{I}$ is equal to:
(a) A (b) 2A (c) 3A (d) 6A

23. The dilute solutions of the electrolytes of same valence type at the same concentrations will have:
(a) Equal ionic strengths (b) Equal activity coefficients (c) Unequal activity coefficients (d) Unequal ionic strengths.
Choose the correct answer(s) with the help of Debye–Hückel limiting law.

EXERCISES

6.1 Show that for n moles of a van der Waals gas

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$$

[*Hint*: Thermodynamic equation of state is $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$.]

6.2 Show that in case of isothermal expansion of n moles of a van der Waals gas, internal energy change,

$$\Delta U = -an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

[*Hint*: $(\partial U/\partial V)_T = an^2/V^2$.]

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6.11 Find out the mean ionic activity ($a_\pm$) and mean molality ($m_\pm$) of the following electrolytes in solution at 25°C: (a) 0.01 m K_2SO_4 ($\gamma_\pm = 0.71$) (b) 0.05 m Ca $(NO_3)_2$ ($\gamma_\pm = 0.54$).

6.12 Calculate the molar freezing point depression constant of water. Given that, enthalpy of fusion of ice at 0°C is 6.01 kJ mol^{-1}.

6.13 Calculate the freezing point of a solution of 10 g of glucose in 70 g of water. Given, $\Delta_{fus}H$, (ice) at 0°C = 6.01 kJ mol^{-1}, and molar mass of glucose = 180.16 g mol^{-1}.

6.14 The osmotic pressure at 25°C of a solution containing 1.56 g of a polymer per 100 mL of solution was found to be 8.95 cm of water. Calculate the molecular weight of the polymer. (Given, $\rho = 1$ g cm^{-3}, $g = 980.67$ cm · s^{-1}).

6.15 A mixture is prepared by dissolving 19 g sucrose, 11 g glucose and 7.3 g urea in 10 dm^3 of water at 25°C. Calculate the osmotic pressure of the solution at 25°C.

6.16 The potential of the cell

$$Cd(s)|CdI_2(a_2)|AgI(s)|Ag(s)$$

is 0.286 volt at 25°C. Calculate the mean ionic activity of the ions in the solution and the activity of the electrolyte. Given that,

$$E^\circ_{Cd^{+2}/Cd} = -0.403 \text{ volt} \quad \text{and} \quad E^\circ_{Ag/AgI/I^-} = -0.1522 \text{ volt}$$

6.17 Find out the value of mean ionic activity coefficient of 0.01 m HCl (aq) at 25°C using Debye–Hückel limiting law.

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Chapter 7

Statistical Thermodynamics

We have so far focussed on the system as a whole, while studying thermodynamics, without caring for the properties of individual atoms and molecules the system is composed of. In thermodynamics, one deals with the average behaviour of the system. For example, the pressure of a gas is interpreted as the average force per unit area exerted by its constituent atoms and molecules and there is no need to specify which particles are striking the wall at any instant.

To focus on individual particles one will have to consider the energies possessed by them. If energy of particles were continuously varying, i.e. the particles can have any value of energy, the task would become formidable because a systems invariably contain Avogadro number of particles and there would be Avagadro number of equations to solve. Fortunately quantum theory helps. According to quantum theory, particles can have only those energies which are permitted by the allowed energy levels. The task now reduces to work out how these particles are distributed amongst the different permitted energy levels. This is what Boltzmann distribution law is about and is the starting point of statistical thermodynamics. The statistical treatment is based on one more important principle: the most probable distribution in a system can be taken to be the equilibrium distribution.

Before we take up the Boltzmann distribution law we should be clear about one thing, that is, the statistical method as a whole. Although, we consider constituent particles, the results obtained are applicable to the system as a whole. In fact it is true of all statistics. Conclusions drawn from statistics are never applicable on individual events. If you have one of your feet on a burning stove and the other in an ice bath, statistics cannot be invoked to conclude that you are comfortable on the average. Secondly while applying statistical method the number of events should be large which is always in physico-chemical systems, where we have Avogadro number of particles.

7.1 THE BOLTZMANN DISTRIBUTION

Before taking up Boltzmann distribution let us introduce the term 'probability of a distribution'. Since most probable distribution is taken to be equilibrium distribution let us see what is meant by the term probability of a distribution. The probability of a given distribution of molecules among energy levels could be defined as the number of ways of realizing the particular distribution divided by

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the total number of possible arrangements. For a given system this total number is some constant, and it is convenient to omit it from the definition of the probability of the system. The new definition, therefore, is: the thermodynamic probability ω of a distribution is equal to the number of ways of realizing the distribution. This was the definition introduced by Boltzmann to relate probability and entropy: $S = k \ln \omega$.[1]

Let us now consider a system of the following specifications:

(i) The system has a fixed energy E and contains fixed number N of identical particles; such a collection of units is called a *microcanonical ensemble.*

(ii) The allowed energy levels for the particles (atoms and molecules etc.) are known from quantum mechanics and are specified as ε_1, ε_2, ⋯

Now let the N distinguishable particles be assigned to the energy levels in such a way that there are N_1 particles in ε_1, N_2 in ε_2 and so on, i.e. in general N_j particles in level ε_j. The probability of any particular distribution, characterized by a particular set of occupation numbers N_j is by definition equal to the number of ways of realizing that distribution.

Since permuting the particles within a given energy level does not produce a new distribution, we can write

$$\omega = \frac{N!}{N_1!\, N_2! \ldots N_j! \ldots} = \frac{N!}{\prod_j N_j!} \tag{7.1}$$

The following two conditions should also hold for the system:

$$\sum N_j = N \tag{7.2a}$$

and

$$\sum N_j \varepsilon_j = E \tag{7.2b}$$

By taking the logarithm of the expression on both the sides of Equation (7.1), we can write

$$\ln \omega = \ln N! - \sum \ln \left(N_j!\right)$$

Using Sterling's approximation for the factorials of large numbers, we therefore, can write

$$\ln N! = N \ln N - N \tag{7.3}$$

or

$$\ln \omega = N \ln N - N - \sum N_j \ln N_j + \sum N_j$$

$$= N \ln N - \sum N_j \ln N_j \tag{7.4}$$

Applying the conditions of maxima and keeping in mind that N is constant, we get

$$\delta \ln \omega = \delta(N \ln N) - \delta\left(\sum N_j \ln N_j\right) = 0$$

1. See Chapter 5, Equation 5.50.

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As N is constant,

$$\delta\left(\sum N_j \ln N_j\right) = 0$$

or

$$\sum\left(\ln N_j\right)\delta N_j + \sum \delta N_j = 0$$

But

$$\sum N_j = N = \text{constant implies,} \quad \sum \delta N_j = 0.$$

Therefore,

$$\sum\left(\ln N_j\right)\delta N_j = 0 \tag{7.5}$$

In view of the two restraints (7.2a) and (7.2b), we can write

$$\delta N = \sum \delta N_j = 0 \tag{7.6a}$$

and

$$\delta E = \sum \varepsilon_j \delta N_j = 0 \tag{7.6b}$$

as N and E are constants. Multiplying Equations (7.6a) and (7.6b) by two arbitrary constants[2] α and β respectively and adding to Equation (7.5), we get

$$\sum \alpha \delta N_j + \sum \beta \varepsilon_j \delta N_j + \sum\left(\ln N_j\right)\delta N_j = 0 \tag{7.7}$$

The variations δN_j may now be considered to be perfectly arbitrary (the restraining conditions having been removed) so that each term of Equation (7.7) in the summation must vanish. Therefore,

$$\ln N_j + \alpha + \beta\varepsilon_j = 0$$

or

$$N_j = \exp(-\alpha)\,\exp(-\beta\varepsilon_j) \tag{7.8}$$

From Equation (7.8), it follows that β should have the dimensions of reciprocal of energy and it has been shown to be equal to $1/(kT)$. Thus

$$N_j = \exp(-\alpha)\,\exp\left(-\frac{\varepsilon_j}{kT}\right) \tag{7.9}$$

It is possible that there may be more than one state corresponding with the energy level ε_j. If this is so the level is said to be *degenerate* and is assigned the statistical weight, g_j, equal to the number of superimposed levels. The distribution law may therefore be generalized as

$$N_j = g_j \exp(-\alpha)\exp\left(-\frac{\varepsilon_j}{kT}\right) \tag{7.10}$$

The constant α can be evaluated using condition (7.2a). Whence

---

2.This is an application of Lagrange's method of undetermined multipliers, the standard treatment of constrained maxima problems.

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$$\sum g_j \exp(-\alpha) \exp\left(-\frac{\varepsilon_j}{kT}\right) = \sum N_j = N$$

or

$$\exp(-\alpha) = \frac{N}{\sum g_j \exp\left[-\varepsilon_j/(kT)\right]}$$

Therefore, Equation (7.10) becomes

$$\frac{N_j}{N} = \frac{g_j \exp\left[-\varepsilon_j/(kT)\right]}{\sum g_j \exp\left[-\varepsilon_j/(kT)\right]} \tag{7.11}$$

This is the *Boltzmann distribution law* in its most general form. The expression $\Sigma g_j \exp[-\varepsilon_j/(kT)]$ in the denominator of Equation (7.11) is important in statistical mechanics. It is called *partition function* and is denoted by the symbol z for the microcanonical ensemble

$$z \equiv \sum_j g_j \exp\left(\frac{-\varepsilon_j}{kT}\right) \tag{7.12}$$

The ratio of number of particles in any two states l and m is

$$\frac{N_l}{N_m} = \frac{g_l \exp\left[-\varepsilon_l/(kT)\right]}{g_m \exp\left[-\varepsilon_m/(kT)\right]}$$

Thus the terms in the summation for z indicate how the particles are partitioned among the various energy states. The average energy $\bar{\varepsilon}$ of a particle is given by

$$\bar{\varepsilon} = \frac{\sum N_j \varepsilon_j}{\sum N_j} = \frac{\sum g_j \varepsilon_j \exp\left[-\varepsilon_j/(kT)\right]}{\sum g_j \exp\left[-\varepsilon_j/(kT)\right]}$$

or

$$\bar{\varepsilon} = kT^2 \frac{\partial \ln z}{\partial T} \tag{7.13}$$

EXAMPLE 7.1 Find out the number of ways of distributing 20 particles when the number of particles in ε_1, ε_2, ε_3, ε_4 and ε_5 energy levels are 4, 4, 6, 3 and 3 respectively.

Solution We get

$$\omega = \frac{N!}{N_1!\, N_2!\, N_3!\, N_4!\, N_5!} = \frac{20!}{4!\,4!\,6!\,3!\,3!} = 1.63 \times 10^{11} \quad \blacksquare$$

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EXAMPLE 7.2 The vibrational frequency of CO molecule is $6.5 \times 10^{13}\ s^{-1}$. Calculate the fraction of molecules present in vibrational level (i) $v = 1$ and (ii) $v = 2$ at 25°C. (Consider zero point energy = 0.)

Solution (i) Energy of $v = 1$ level is

$$\varepsilon_1 = h\nu = 6.627 \times 10^{-34}\ \text{J}\cdot\text{s} \times 6.5 \times 10^{13}\ \text{s}^{-1} = 4.31 \times 10^{-20}\ \text{J}$$

Then

$$\frac{\varepsilon_1}{kT} = \frac{4.31 \times 10^{-20}\ \text{J}}{1.381 \times 10^{-23}\ \text{JK}^{-1} \times 298\ \text{K}} = 10.473$$

and

$$\frac{N_1}{N} = \frac{g_1 \exp\left[-\varepsilon_1/(kT)\right]}{\sum_j g_j \exp\left[-\varepsilon_j/(kT)\right]}$$

$$= \frac{e^{-10.473}}{e^{-0/kT} + e^{-10.473} + \cdots}$$

$$\approx e^{-10.473}$$

$$= 2.83 \times 10^{-5}$$

Here g_j is considered to be 1.

(ii) Considering harmonic oscillator, we have

$$\varepsilon_2 = 2h\nu = 2 \times 4.31 \times 10^{-20}\ \text{J} = 8.62 \times 10^{-20}\ \text{J}$$

Then

$$\frac{\varepsilon_2}{kT} = 20.946$$

and

$$\frac{N_2}{N} = \frac{e^{-20.946}}{e^{-0/(kT)} + e^{-10.473} + e^{-20.946}} \approx e^{-20.946} = 8 \times 10^{-10} \qquad \blacksquare$$

EXAMPLE 7.3 Calculate the ratio of number of particles per state for two states separated by an energy 4.3×10^{-20} J for (a) $T = 0$ K and (b) $T = 300$ K.

Solution If l and m are these two states, then

$$\frac{N_l/g_l}{N_m/g_m} = \frac{\exp\left[-\varepsilon_l/(kT)\right]}{\exp\left[-\varepsilon_m/(kT)\right]} = \exp\left[-\frac{(\varepsilon_l - \varepsilon_m)}{kT}\right]$$

Here N_l/g_l or N_m/g_m is the number of particles per state, and $(\varepsilon_l - \varepsilon_m)$ is the energy difference between states l and m.

$$\text{(a)}\ \frac{N_l/g_l}{N_m/g_m} = \exp\left(-\frac{4.3 \times 10^{-20}\ \text{J}}{1.381 \times 10^{-23}\ \text{JK}^{-1} \times 0}\right) = e^{-\infty} = 0$$

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(b) $$\frac{N_l/g_l}{N_m/g_m} = \exp\left(-\frac{-4.3 \times 10^{-20}\,\text{J}}{1.381 \times 10^{-23}\,\text{JK}^{-1} \times 300\,\text{K}}\right) = e^{-10.38} = 3.10 \times 10^{-5}$$ ■

EXAMPLE 7.4 At 0°C and atmospheric pressure, a cubic metre of atomic hydrogen contains about 3×10^{25} hydrogen atoms. Calculate the number of atoms in first-excited singlet state, i.e. in $n = 2$ state at 273 K and at 14273 K.

Solution We know that the ratio between the number of atoms in $n = 1$ and $n = 2$ states is

$$\frac{n_2}{n_1} = \frac{g_2 \exp\left[-\varepsilon_2/(kT)\right]}{g_1 \exp\left[-\varepsilon_1/(kT)\right]} = \frac{g_2}{g_1} \exp\left(-\frac{\varepsilon_2 - \varepsilon_1}{kT}\right)$$

Total number of possible states corresponds to the quantum number n is equal to $2n^2$. In $n = 1$ state, a 1-s electron has $l = 0$ and $m_l = 0$, but $m_s = \pm 1/2$. Therefore, the total number of states of energy ε_1 is 2. In $n = 2$ state, a 2-s ($l = 0$) electron has $m_s = \pm 1/2$ and a 2-p ($l = 1$) electron has $m_l = 0, \pm 1$ with $m_s = \pm 1/2$ in each case. Therefore, the total number of states with energy $\varepsilon_2 = 8$.

The energy of ground state $\varepsilon_1 = -13.6$ eV and the energy of $n = 2$ state,

$$\varepsilon_2 = \frac{\varepsilon_1}{n^2} = -\frac{13.6}{4}\,\text{eV} = -3.4\,\text{eV}$$

Therefore,

$$\frac{\varepsilon_2 - \varepsilon_1}{kT} = \frac{(-3.4 + 13.6)\,\text{eV}}{8.617 \times 10^{-5}\,\text{eV K}^{-1} \times 273\,\text{K}} = \frac{10.2}{0.0235} = 434.04$$

and

$$\frac{n_2}{n_1} = \frac{8}{2} e^{-434.04} = 1.3 \times 10^{-188}$$

Hence, almost one atom is present in $n = 2$ state for 10^{188} atoms are present in $n = 1$ state. Thus, for total 3×10^{25} atoms we can say that all are present at ground state.

Now, at 14273 K,

$$\frac{\varepsilon_2 - \varepsilon_1}{kT} = \frac{10.2\,\text{eV}}{8.617 \times 10^{-5}\,\text{eV K}^{-1} \times 14273} = 8.29$$

and

$$\frac{n_2}{n_1} = \frac{8}{2} e^{-8.29} = 1 \times 10^{-3}$$

Thus for 3×10^{25} atoms, number of atoms present in $n = 2$ is 3×10^{22}. ■

EXAMPLE 7.5 At what temperature would the population of the states at a higher energy be (1/1000)th that of the states at a lower energy if the difference in energy is 8×10^{-20} J?

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Solution The ratio between the population of two states is

$$\frac{N_l/g_l}{N_m/g_m} = \exp\left(-\frac{\varepsilon_l - \varepsilon_m}{kT}\right)$$

or

$$\frac{1}{1000} = \exp\left(-\frac{8\times10^{-20}\ \text{J}}{1.381\times10^{-23}\ \text{JK}^{-1}\,T}\right)$$

Therefore, $T = 838.4$ K. ■

EXAMPLE 7.6 A system containing N identical molecules is cooled to 0 K. If the energy levels are not degenerate, then calculate the entropy of the system. Also, calculate the entropy of the system if the degeneracy of each energy level is 2.

Solution At 0 K, N molecules will be present in the lowest energy state. Therefore,

$$S = k\ln\omega = k\ln\frac{N!}{N!\,0!\,0!} = k\ln 1 = 0$$

This is also true according to the third law of thermodynamics. Thus the assignment of the value zero to the entropy at 0 K for a system with a non-degenerate lowest energy level is consistent with Boltzmann principle. When the degeneracy of each energy level is 2, then each molecule can be present in 2 states. Then

$$S = k\ln 2^N = Nk\ln 2 = R\ln 2 = 5.76\ \text{JK}^{-1}\ \text{mol}^{-1}$$

This is called *residual entropy*. Even at 0 K, the system has certain entropy. The lowest energy level of CO and N_2O are degenerate. Each molecule can be present in two states. This is the basis of occurrence of a residual entropy at 0 K in CO and N_2O. ■

7.2 INTERNAL ENERGY AND HEAT CAPACITY

Thermodynamics does not deal with individual particles. It deals with large-scale systems containing large number of particles—Avogadro number of particles. Consider now an ensemble of large number of systems, each containing a mole of substance, at constant temperature and volume. The average energy of these systems will be the usual molar internal energy $\bar{E}$. A collection of systems of this kind is called a *canonical ensemble*.

Replacing each particle by the whole system and considering that the allowed energies of the whole system are $E_1, E_2, \ldots, E_j$, and using Equation (7.13), we can write for average energy $\bar{E}$ as

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$$\bar{E} = \frac{\sum N_j E_j}{\sum N_j} = \frac{\sum g_j E_j \exp\left[-E_j/(kT)\right]}{\sum g_j \exp\left[-E_j/(kT)\right]}$$

Writing

$$Z \equiv \sum g_j \exp\left(-\frac{E_j}{kT}\right) \tag{7.14}$$

we have

$$\bar{E} = kT^2 \frac{\partial \ln Z}{\partial T} \tag{7.15}$$

where Z is the partition function for the canonical ensemble.

From Equation (7.15), it follows that

$$\bar{C}_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(kT^2 \frac{\partial \ln Z}{\partial T}\right)_V = \frac{k}{T^2} \frac{\partial^2 \ln Z}{\partial (1/T)^2} \tag{7.16}$$

Equation (7.16) is the relationship between $\bar{C}_V$ and the canonical partition function.

7.3 STATISTICAL MECHANICAL FORMULATION OF THE THIRD LAW

Equation (7.16) can be utilized to calculate entropy in terms of partition function. Thus:

$$\begin{aligned} S - S_0 &= \int_0^T \frac{C_V}{T} dT \\ &= \int_0^T \frac{1}{T} \frac{\partial}{\partial T}\left(kT^2 \frac{\partial \ln Z}{\partial T}\right)_V dT \\ &= kT\left(\frac{\partial \ln Z}{\partial T}\right)_V + k \int_0^T \left(\frac{\partial \ln Z}{\partial T}\right)_V dT \end{aligned}$$

or

$$S - S_0 = \frac{\bar{E}}{T} + k \ln Z - k \ln Z \,|_{\text{at } T=0} \tag{7.17}$$

In Equation (7.17) only S_0 and $|k \ln Z|_{T=0}$ are temperature-independent terms. The constant term S_0, the entropy at absolute zero, is therefore

$$S_0 = k \ln Z \,|_{T=0} = k \ln g_0 \tag{7.18}$$

where g_0 is the statistical weight of the lowest possible energy state of the system. Equation (7.18) is the statistical mechanical formulation of the third law.

In a perfect crystal, there will usually be one and only one arrangement of its constituent atoms at absolute zero, i.e. the statistical weight $g_0 = 1$ and hence

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according to Equation (7.18) at absolute zero of temperature $S_0 = 0$. In view of these facts, Equation (7.17) reduces to

$$S = \frac{\overline{E}}{T} + k \ln Z \tag{7.19}$$

Equation (7.19) can also be deduced from the Boltzmann equation, $S = k \ln \omega$ [Equation (5.50) in Chapter 5]. Using Equation (7.1) and the Stirling approximation, we can write

$$S = k(N \ln N - N) - k \sum (N_j \ln N_j - N_j)$$

Substituting

$$N_j = \frac{N \exp\left[-\varepsilon_j/(kT)\right]}{z}$$

We find that

$$S = k(N \ln N - N) - kN\left(\ln N - \ln z - 1 - \frac{\overline{\varepsilon}}{kT}\right) = \frac{N\overline{\varepsilon}}{T} + kN \ln z$$

If N is equal to L (the Avogadro number), the expression for molar entropy $\overline{S}$ can be written as

$$\overline{S} = \frac{\overline{E}}{T} + k \ln z^L$$

which is the same as Equation (7.19) provided $Z = z^L$, the justification for which will be provided in Section 7.5.

7.4 FREE ENERGY AND WORK FUNCTION IN TERMS OF PARTITION FUNCTION

Substituting the value of S from Equation (7.19) in the equation for work function $A = E - TS$ [refer to Equation (5.90) in Chapter 5], we get

$$A = -kT \ln Z \tag{7.20}$$

and the pressure

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T \tag{7.21}$$

Similarly one can write the expression for Gibb's free energy G, using the relationship $G = A + PV$ and from ΔG° the equilibrium constant for a reaction can be calculated. The expression for enthalpy can easily be deduced using the relationship $H = E + PV$.

It has now been shown that all thermodynamic properties of interest are related to partition function Z. Once we know how to evaluate the partition function these properties can be calculated.

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7.5 EVALUATION OF PARTITION FUNCTIONS

In many cases, for example, in the case of a crystal composed of independent oscillators or of an almost perfect gas in which intermolecular forces were negligible, it is a good approximation to consider that E_j an energy of the system, can be represented as sum of energies ε_j of non-interacting individual particles. In such cases, we can write

$$E_j = \varepsilon_1(1) + \varepsilon_2(2) + \varepsilon_3(3) + \cdots + \varepsilon_L(L) \tag{7.22}$$

Equation (7.22) indicates that particle (1) occupies energy level ε_1, particle (2) occupies energy level ε_2, etc. Each different way of assigning the particles to the energy levels determines a distinct state of the system, E_j. The partition function then becomes

$$Z = \sum_j \exp\left(\frac{-E_j}{kT}\right) = \sum_j \exp\left[-\frac{\varepsilon_j(1)+\varepsilon_j(2)+\cdots+\varepsilon_j(L)}{kT}\right]$$

The statistical weights g_j are omitted for convenience. The second summation is taken over all the different ways of assigning the particles to energy levels ε_j. It can be rewritten as

$$\sum_j \exp\left[-\frac{\varepsilon_j(1)}{kT}\right] \exp\left[-\frac{\varepsilon_j(2)}{kT}\right] \cdots \exp\left[-\frac{\varepsilon_j(L)}{kT}\right]$$

Since each particle has the same set of allowed energy levels, this sum is equal to

$$Z = \left[\sum_j \exp\left(-\frac{\varepsilon_j}{kT}\right)\right]^L = z^L$$

The above relationship between the canonical and microcanonical partition functions applies to the case in which rearranging the particles among the energy levels in Equation (7.22) actually gives rise to different states that must be included in the summation for Z. This is the situation in a perfect crystal, where different particles (oscillators) occupy distinct sites at different locations in the crystal structure. In the case of a gas, on the contrary there are no such distinct labelled sites and each molecule is free to move throughout the entire available volume. States in the gas which differ merely by the interchange of two particles are not distinguishable and therefore should be counted only once. If each level in Equation (7.22) contains only one particle, the number of permutations of the particles among the levels is $L!$. We therefore divide the expression for Z by this factor obtaining for ideal gas case, $Z = z^L/(L!)$. Thus for ideal crystals,

$$Z = z^L \tag{7.23a}$$

and for ideal gas

$$Z = \frac{z^L}{L!} \tag{7.23b}$$

In other words, Equation (7.23a) is for distinguishable entities and

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Equation (7.23b) for indistinguishable entities. Intermediate kind of systems like imperfect gases and liquids represent difficult situations because they cannot be treated as ensembles of non-interacting particles.

To calculate the partition functions for an ideal gas, it is often convenient to assume that the energy of a molecule is the sum of translation, rotational, vibrational and electronic terms. Thus,

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e \tag{7.24}$$

Therefore, the partition function is the product of corresponding terms,

$$z = z_t z_r z_v z_e \tag{7.25}$$

7.5.1 Monatomic Gases

The simplest case of monatomic gases is that in which there are no rotational or vibrational degrees of freedom and rarely any electronic excitation, except at very high temperatures. It is known from quantum mechanics that the translational energy levels for a particle of mass m, in a one-dimensional box, are given by $\varepsilon_n = n^2h^2/(8ma^2)$, where n is the quantum number and h is the Planck constant. The statistical weight of each level is unity, $g_n = 1$. Therefore, the partition function z becomes

$$z = \sum \exp\left[-\frac{n^2h^2/(8ma^2)}{kT}\right]$$

The energy levels are so closely packed together that they can be taken to be continuous and the summation can be replaced by an integration,

$$z = \int_0^\infty \exp\left[-\frac{n^2h^2/(8ma^2)}{kT}\right] dn$$

Putting

$$x^2 = \frac{n^2h^2/(8ma^2)}{kT}$$

we get

$$z = \frac{a}{h}(8mkT)^{1/2} \int_0^\infty \exp(-x)^2\, dx = \frac{(2\pi mkT)^{1/2}\, a}{h} \tag{7.26}$$

For three degrees of translational freedom, this expression is cubed, and since $a^3 = V$, we obtain

$$z = \frac{(2\pi mkT)^{3/2}\, V}{h^3} \tag{7.27}$$

The canonical partition function Z can therefore be written as

$$Z = \frac{1}{L!} z^L = \frac{1}{L!}\left[\frac{(2\pi mkT)^{3/2}\, V}{h^3}\right]^L \tag{7.28}$$

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The energy, therefore, is

$$\bar{E} = LkT^2 \frac{\partial \ln z}{\partial T} = RT^2 \frac{\partial \ln z}{\partial T} = \frac{3}{2}RT \text{ (see Example 7.7)}$$

According to Stirling formula, i.e. $L! = (L/e)^L$. Thus,

$$Z = \left(\frac{2\pi mkT^{3/2}eV}{Lh^3}\right)^L$$

or

$$\ln Z = L \ln \left[\frac{eV}{Lh^3}(2\pi mkT)^{3/2}\right]$$

and the entropy from Equation (7.19) is

$$\bar{S} = \frac{3}{2}R + R \ln \frac{eV}{Lh^3}(2\pi mkT)^{3/2}$$

or

$$\bar{S} = R \ln \frac{e^{5/2}V}{Lh^3}(2\pi mkT)^{3/2} \quad [\text{as } \ln e = 1] \tag{7.29}$$

Equation (7.29) is the well-known *Sackur–Tetrode equation.*

EXAMPLE 7.7 Show that the translational energy of a gas is (3/2)*RT* per mole

Solution We know that

$$\bar{E} = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V$$

Since $Z = z^L/(L!)$

$$\bar{E} = kT^2 \left(\frac{\partial}{\partial T} \ln \frac{z^L}{L!}\right)$$

Using Stirling's formula, $\ln L! = L \ln L - L$, we get

$$\bar{E} = LkT^2 \left(\frac{\partial \ln z}{\partial T}\right)_V$$

Since

$$z_t = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

we get

$$\left(\frac{\partial \ln z_t}{\partial T}\right)_V = \frac{3}{2T}$$

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Hence

$$\bar{E}_t = LkT^2 \frac{3}{2T} = \frac{3}{2} RT \text{ per mole} \quad \blacksquare$$

EXAMPLE 7.8 Making use of the expression for the translational partition function, derive the ideal gas equation between P, V and T for one mole of the gas.

Solution We know from Equation (7.20)

$$A = -kT \ln Z$$

Since $Z = z^L/(L!)$, we have

$$\ln Z = L \ln z - L \ln L + L$$

We also know that

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

Therefore,

$$P = kT \left[L \left(\frac{\partial \ln z}{\partial V} \right)_T \right]$$

Since

$$z_t = \left(\frac{2\pi mkT}{h^3} \right)^{3/2} V$$

we get

$$\left(\frac{\partial \ln z_t}{\partial V} \right)_T = \frac{1}{V}$$

Hence

$$P = LkT \left(\frac{\partial \ln z_t}{\partial V} \right)_T = \frac{LkT}{V} = \frac{RT}{V}$$

or $PV = RT$ for one mole of gas. $\blacksquare$

EXAMPLE 7.9 Calculate the translational partition function of an oxygen molecule confined in a 1-litre vessel at 27°C.

Solution We know that

$$z_t = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

$$m_{O_2} = 32 \times 1.66 \times 10^{-27} \text{ kg}$$

$$V = 1 \text{ litre} = 1000 \text{ cm}^3 = 1000 \ (10^{-2} \text{ m})^3 = 10^{-3} \text{ m}^3$$

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Therefore,

$$z_t = \frac{\left[2 \times 3.14 \times \left(32 \times 1.66 \times 10^{-27}\ \text{kg}\right)\left(1.381 \times 10^{-23}\ \text{JK}^{-1}\right) \times (300\ \text{K})\right]^{3/2} 10^{-3}\ \text{m}^3}{\left(6.626 \times 10^{-34}\ \text{Js}\right)^3}$$

$$= 5.328 \times 10^{33}$$

Thus about 5×10^{33} quantum level are thermally accessible for the oxygen molecule at 27°C. ■

EXAMPLE 7.10 Using the expression for translational partition function derive an expression for translation enthalpy of an ideal gas and show that its value is (5/2) *RT* per mole of the gas. Using this result compute the value of translational heat capacity at constant pressure.

Solution We know that

$$H = E + PV$$

Substituting the values of E and P in terms of translational partition function, we get

$$H_t = kT^2\left(\frac{\partial \ln Z_t}{\partial T}\right)_V + kTV\left(\frac{\partial \ln Z_t}{\partial T}\right)_T$$

since

$$Z_t = \frac{z_t^L}{L!} \quad \text{and} \quad z_t = \frac{(2\pi mkT)^{3/2} V}{h^3}$$

We have

$$\left(\frac{\partial \ln Z_t}{\partial T}\right)_V = \frac{3L}{2T} \quad \text{and} \quad \left(\frac{\partial \ln Z_t}{\partial V}\right)_T = \frac{L}{V}$$

Therefore,

$$H_t = \frac{3LkT^2}{2T} + \frac{kTVL}{V} = \frac{3}{2}LkT + LkT = \frac{5}{2}RT \text{ per mole}$$

and

$$(C_P)_t = \left(\frac{\partial H_t}{\partial T}\right)_P = \frac{5R}{2} \text{ per mole} \quad ■$$

EXERCISE 7.11 Derive expression for translational Gibbs free energy for an ideal gas.

Solution We have

$$A_t = -kT \ln Z_t \quad \text{and} \quad G_t = A_t + PV$$

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Since

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

we get

$$G_t = -kT \ln Z_t + kTV\left(\frac{\partial \ln Z_t}{\partial V}\right)_T$$

Also, since

$$Z_t = \frac{z_t^L}{L!}, \qquad z_t = \frac{(2\pi mkT)^{3/2} V}{h^3}, \qquad \ln L! = L \ln L - L$$

One can obtain the value of G_t by making appropriate substitutions. Thus

$$G_t = -RT \ln\left[\frac{(2\pi mkT)^{3/2}}{h^3}\frac{V}{L}\right]$$

Since for an ideal gas

$$\frac{V}{L} = \frac{kT}{P}$$

We have

$$G_t = -RT \ln\left[\frac{(2\pi mkT)^{3/2}}{h^3}\frac{kT}{P}\right] \text{ per mole} \quad \blacksquare$$

EXAMPLE 7.12 Calculate the entropy of argon at 273 K and one atmospheric pressure, using the following data:

$R = 1.99$ cal/K, $e = 2.718$, $V = 22414$ cc, $L = 6.023 \times 10^{23}$, $h = 6.62 \times 10^{-27}$ erg sec, $\pi = 3.1416$, $m = 6.63 \times 10^{-23}$ g, $k = 1.38 \times 10^{-16}$ erg K^{-1}, and $T = 273.2$ K.

Solution Substituting these values in Equation (7.29), the value of entropy works out to be 36.99 cal degree^{-1} mol^{-1} which agrees with the third law value, 36.95. $\blacksquare$

EXAMPLE 7.13 Making use of expression for translational partition function deduce expressions for the entropy change per mole (i) when an ideal gas expands isothermally from an initial volume V_1 to a final volume V_2, and (ii) when the ideal gas is heated as well as allowed to expand from an initial state (T_1, V_1) to a final state (T_2, V_2).

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Solution Case (i) is an isothermal expansion, where

$$\begin{aligned}\Delta S &= S(T, V_2) - S(T, V_1) \\ &= R \ln \frac{e^{5/2} V_2}{Lh^3} (2\pi mkT)^{3/2} - R \ln \frac{e^{5/2} V_1}{Lh^3} (2\pi mkT)^{3/2} \\ &= R \ln \left(\frac{V_2}{V_1} \right)\end{aligned}$$

In case (ii),

$$\begin{aligned}\Delta S &= R \ln \frac{e^{5/2} V_2}{Lh^3} (2\pi mkT_2)^{3/2} - R \ln \frac{e^{5/2} V_1}{Lh^3} (2\pi mkT_1)^{3/2} \\ &= R \ln \left(\frac{T_2}{T_1} \right)^{3/2} + R \ln \frac{V_2}{V_1} \quad \blacksquare\end{aligned}$$

7.5.2 Diatomic Molecule—Rotational Partition Function

The permitted energy levels for diatomic molecules according to rigid-rotor model, as obtained from quantum mechanics are given as

$$\varepsilon_r = \frac{J(J+1)h^2}{8\pi^2 I}$$

where J is the rotational quantum number and I is the moment of inertia of the molecule. If the moment of inertia is sufficiently high, the energy levels become so closely spaced as to be practically continuous.

Some consideration is required for the statistical weight of a rotational level J. The number of ways of distributing J quanta of rotational energy between two axes of rotation equals $2J + 1$, because in every case except $J = 0$, there are two possible alternatives for each added quantum. The statistical weight of a rotational level J is, therefore, $2J + 1$.

The rotational partition function can now be written as

$$z_r = \sum (2J+1) \exp \left[-J(J+1) \frac{h^2}{8\pi^2 IkT} \right] \tag{7.30}$$

Since the energy levels are closely space, the summation has to be replaced by integration. Therefore,

$$z_r = \int_0^\infty (2J+1) \exp \left[-J(J+1) \frac{h^2}{8\pi^2 IkT} \right] dJ$$

or

$$z_r = \frac{8\pi^2 IkT}{h^2} \tag{7.31}$$

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In view of symmetry properties of diatomic molecules a symmetry number σ is introduced, in Equation (7.31) which is either $\sigma = 1$ (heteronuclear diatomic molecules) or $\sigma = 2$ (homonuclear diatomic molecules).

$$z_r = \frac{8\pi^2 IkT}{\sigma h^2} \tag{7.32}$$

The expression for rotational entropy can now be obtained using Equation (7.19). Therefore,

$$\bar{S}_r = RT\frac{\partial \ln z_r}{\partial T} + k \ln z_r^L = R + R \ln z_r = R + R \ln \frac{8\pi^2 IkT}{\sigma h^2}$$

Rotational contribution to other thermodynamic function can be evaluated as follows:

Rotational energy

We know that

$$E_r = kT^2 \left(\frac{\partial \ln Z_r}{\partial T}\right)_V \quad \text{and} \quad Z_r = z_r^L$$

Therefore,

$$\left(\frac{\partial \ln Z_r}{\partial T}\right)_V = L\left(\frac{\partial \ln z}{\partial T}\right)_V$$

In view of Equation (7.32), we can write

$$\left(\frac{\partial \ln z}{\partial T}\right)_V = \frac{1}{T}$$

Therefore, $E_r = LkT = RT$, when L = Avogadro's number. Therefore for 1 mol of substance, $E_r = \bar{E}_r$ (molar) and therefore $\bar{E}_r$ (molar) = RT and consequently C_V (rotational) = R per mol.

Rotational enthalpy

We have

$$H_r = E_r + PV = LkT + VLkT\left(\frac{\partial \ln z}{\partial V}\right)_T$$

Since z is not a function of V, the second term in the right-hand side of the above equation equals zero. Therefore, $H_r = LkT$. When L = Avogadro's number, $H_r = \bar{H}_r$ (molar). Therefore $\bar{H}_r$ (molar) = RT and consequently C_P (rotational) = R per mole.

Rotational entropy

We know that

$$S_r = \frac{\bar{E}_r}{T} + k \ln z_r^L = R + Lk \ln z_r$$

Substituting value z from Equation (7.32), we get

$$\bar{S}_r = R \ln \left(\frac{e 8\pi^2 IkT}{\sigma h^2}\right) \text{ per mole}$$

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Rotational free energy and work function

Rotational free energy G_r and work function A_r can be evaluated using equations

$$G_r = H_r - TS_r$$

and $A_r = E_r - TS_r$ and making appropriate substitutions. Thus

$$\bar{G}_r = -RT \ln\left(\frac{8\pi^2 IkT}{\sigma h^2}\right) \text{ per mole}$$

and

$$\bar{A}_r = -RT \ln\left(\frac{8\pi^2 IkT}{\sigma h^2}\right) \text{ per mole}$$

Therefore, $\bar{S} = \bar{S}_r + \bar{S}_{tr}$ provided the vibrational contribution is small, $\bar{S}_{tr}$ can be computed using Equation (7.29).

EXAMPLE 7.14 Calculate the rotational entropy and free energy for oxygen gas at 25°C and one atmosphere pressure, the moment of inertia of O_2 gas is 1.9373×10^{-46} kg m^2. Given that $h = 6.626 \times 10^{-34}$ Js, Boltzmann constant $k = 1.38 \times 10^{-23}$ JK^{-1}, $\pi = 3.1416$, $\sigma = 2$ and $R = 8.314$ JK^{-1} mol^{-1}.

Solution We have

$$S_r = R + R \ln \frac{8\pi^2 IkT}{\sigma h^2}$$

Making appropriate substitutions the value of rotational entropy work out to be 43.828 JK^{-1} per mole. Similarly the value of G_r can be worked out by making appropriate substitutions in the equation

$$G_r = -RT \ln \frac{8\pi^2 IkT}{\sigma h^2}$$

Thus the value of G_r works out to be −10.583 kJ per mole. ■

7.5.3 Vibrational Partition Function

The permitted vibrational energy levels, according to the harmonic oscillator model, are given by the equation

$$\varepsilon_v = \left(v + \frac{1}{2}\right)h\nu \tag{7.33}$$

where v (0, 1, 2, etc.) are the vibrational quantum numbers. At a low temperature, vibrational contributions are usually small and this approximation is adequate; for calculations at higher temperatures the anharmonicity of vibrations must be considered.

According to Equation (7.12), the partition function for each vibrational degree of freedom is given by

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$$z_v = \sum_v \exp\left[-\left(v+\frac{1}{2}\right)\frac{h\nu}{kT}\right] = \exp\left(-\frac{h\nu}{2kT}\right)\sum_v \exp\left(-\frac{vh\nu}{kT}\right) \tag{7.34}$$

or

$$z_v = \frac{\exp\left[-h\nu/(2kT)\right]}{1-\exp\left[-h\nu/(kT)\right]} \tag{7.35}$$

The total vibrational partition function is the product of terms like Equation (7.35), one for each of the normal modes of vibration of the molecule. That is,

$$Z_v = \prod_j Z_{v,j} \tag{7.36}$$

The vibrational energy from Equations (7.15), (7.23a) and (7.35) is

$$\bar{E} = RT^2\frac{\partial \ln z}{\partial T} = L\frac{h\nu}{2} + \frac{Lh\nu\,\exp\left[-h\nu/(kT)\right]}{1-\exp\left[-h\nu/(kT)\right]}$$

The zero-point energy per mole $\bar{E}_0$ is $Lh\nu/2$. Writing $h\nu/(kT) = x$, we have

$$\frac{\bar{E}-\bar{E}_0}{T} = \frac{Rxe^{-x}}{1-e^{-x}} \tag{7.37}$$

and the heat capacity

$$\left(\frac{\partial E}{\partial T}\right) = C_{V(\text{vibration})} = \frac{Rx^2}{2(\cosh x - 1)} \tag{7.38}$$

From Equation (7.20), since, for the vibrational contribution $A = G$;

$$\frac{\bar{G}-\bar{E}_0}{T} = R\ln\left(1-e^{-x}\right) \tag{7.39}$$

It is evident from Equation (7.21) that $P = 0$ as Z is not a function of V. Therefore,

$$G = A + PV = A$$

and contribution to entropy is

$$\bar{S} = \frac{\bar{E}-\bar{E}_0}{T} - \frac{\bar{G}-\bar{E}_0}{T} \tag{7.40}$$

EXAMPLE 7.15 Calculate the vibrational contribution to the entropy of F_2 at 25°C. Given that the fundamental vibration frequency $\bar{\nu} = 892.1\ \text{cm}^{-1}$, $h = 6.62 \times 10^{-27}$ erg · s and $k = 1.38 \times 10^{-16}\ \text{erg K}^{-1}$.

Solution We know that

$$x = \frac{h\nu}{kT} = \frac{hc\bar{\nu}}{kT}$$

where c is the velocity of light ($c = 3 \times 10^{10}\ \text{cm s}^{-1}$). Therefore,

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$$x = \frac{\left(6.62\times10^{-27}\right)\times\left(3\times10^{10}\right)(892.1)}{\left(1.38\times10^{-16}\right)(273+25)} = 4.305$$

From Equation (7.37), we also have

$$\frac{\bar{E}-\bar{E}_0}{T} = \frac{Rxe^{-x}}{1-e^{-x}} = 0.1196$$

and from Equation (7.39), we get

$$\frac{\bar{G}-\bar{E}_0}{T} = R\ \ln\ (1-e^{-x}) = -0.0279$$

Therefore, from Equation (7.40),

$$\bar{S} = 0.1196+0.0279 = 0.1475\ \text{ cal/deg} \quad \blacksquare$$

7.6 EQUILIBRIUM CONSTANT FOR IDEAL GAS REACTIONS

Let us start with the well-known relationship

$$\Delta G^\circ = -RT\ln K_P \tag{7.41}$$

between the standard free energy change ΔG° and the equilibrium constant K_P. From Equations (7.20) and (7.23b), we have

$$\bar{A} = -kT\ln Z = -kT\ln\left(\frac{z^L}{L!}\right)$$

Since

$$\bar{G} = \bar{A}+P\bar{V} = \bar{A}+RT \quad \text{and} \quad \ln L! = L\ln L - L \ \text{(Stirling formula)} \tag{7.42}$$

we can write

$$\bar{G} = -RT\ln\left(\frac{z}{L}\right) \tag{7.43}$$

Let us write for the partition function z

$$z = z_{\text{int}}\frac{\left(2\pi mkT\right)^{3/2}\bar{V}}{h^3} \tag{7.44}$$

where z_{int} is the product of the non-translational contributions to z, i.e. $z_{\text{int}} = z_r \cdot z_v \cdot z_e$. If we consider one mole of gas in its standard state of $P = 1$ atm, we can write

$$\bar{V} = RT$$

and therefore we can write from Equation (7.44)

$$z^\circ = z_{\text{int}}\frac{\left(2\pi mkT\right)^{3/2}}{h^3}RT \tag{7.45}$$

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for z°, the partition function of an ideal gas in the standard state. From Equation (7.43),

$$\bar{G}^\circ = -RT \ln \frac{z^\circ}{L} \tag{7.46}$$

Now let us consider a simple monomolecular isomerization reaction $A \rightleftharpoons B$ and keep in view two sets of energy levels, $\varepsilon_j(A)$ belonging to A and $\varepsilon_j(B)$ belonging to B. The difference in the energies of the A and B states of the lowest energy is

$$\Delta\varepsilon_0 = \varepsilon_0(B) - \varepsilon_0(A) \tag{7.47}$$

When the reaction reaches equilibrium, the molecules of A will be distributed in accordance with a Boltzmann distribution in the energy levels $\varepsilon_j(A)$ and similarly the molecules of B in the energy levels $\varepsilon_j(B)$.

If we take the zero level of energy for the entire system as the lowest energy level of the A molecules, the partition function of A is simply

$$z_A = \sum_{j=0}^{\infty} \exp\left[-\frac{\varepsilon_j(A)}{kT}\right]$$

In order to discuss equilibrium between A and B we must count the energy levels of B from the same zero level as that used for A. Thus

$$z_B = \sum_{j=0}^{\infty} \exp\left\{\frac{-\left[\varepsilon_j(B) + \Delta\varepsilon_0\right]}{kT}\right\} = \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right)\sum_{j=0}^{\infty} \exp\left[-\frac{\varepsilon_j(B)}{kT}\right]$$

Having assigned a common zero level for energies we can obtain, using Equation (7.46), the statistical expression for the equilibrium constant of the reaction $A \rightleftharpoons B$,

$$-RT \ln K_P = \Delta G^\circ = -RT \ln \frac{z_B^\circ/L}{z_A^\circ/L} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right)$$

or

$$K_P = \frac{z_B^\circ}{z_A^\circ} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right)$$

The reaction $A \rightleftharpoons B$ considered above is a special case, where the change in the number of moles on reaction is zero; $\Delta n = 0$. However, for a more general case $aA + bB \rightleftharpoons cC + dD$. It is easy to see that the expression for K_P will get modified to read

$$K_P = \frac{\left(z_C^\circ/L\right)^c \left(z_D^\circ/L\right)^d}{\left(z_A^\circ/L\right)^a \left(z_B^\circ/L\right)^b} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right) \tag{7.48}$$

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Given the zero-point vibration frequencies are:

$$\left.\begin{aligned} {}^{16}O^{18}O, \quad & \bar{\nu}_0 = 1535.8\ \text{cm}^{-1} \\ {}^{16}O_2, \quad & \bar{\nu}_0 = 1580.4\ \text{cm}^{-1} \\ {}^{18}O_2, \quad & \bar{\nu}_0 = 1490.0\ \text{cm}^{-1} \end{aligned}\right\}$$

Solution From Equation (7.48),

$$K_P = \frac{\left[z^\circ\left({}^{16}O^{18}O\right)\right]^2}{\left[z^\circ\left({}^{16}O_2\right)\right]\left[z^\circ\left({}^{18}O_2\right)\right]} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right) \tag{7.50}$$

where

$$\Delta\varepsilon_0 = \frac{1}{2}hc\left[2(1535.8) - 1580.4 - 1490.0\right] = 1.19 \times 10^{-16}\ \text{erg}$$

then

$$\frac{\Delta\varepsilon_0}{kT} = 0.029$$

Inserting the expression for partition function into Equation (7.50), we get

$$K_P = \frac{m^3\left({}^{16}O^{18}O\right)}{m^{3/2}\left({}^{16}O_2\right)m^{3/2}\left({}^{18}O_2\right)} \frac{\mu^2\left({}^{16}O^{18}O\right)\times 4}{\mu\left({}^{18}O_2\right)\mu\left({}^{16}O_2\right)} \frac{z_\vartheta^2\left({}^{16}O^{18}O\right)}{z_\vartheta\left({}^{18}O_2\right)z_\vartheta\left({}^{16}O_2\right)} \exp\left(-\frac{\Delta\varepsilon_0}{kT}\right) \tag{7.51}$$

The internuclear distances in the isotopic molecules are the same. However the symmetry number $\sigma = 2$ which occurs in the rotational partition functions for the homonuclear diatomic molecules, but not in ${}^{16}O^{18}O$. This leads to the factor of 4 in the term from the ratio of vocational partition functions. Introducing numerical values into Equation (7.51) we find for the value of K_P at 25°C. ■

$$K_P = \frac{34^3}{32^{3/2}\times 36^{3/2}} \frac{(16\times 18/34)^2\times 4}{9\times 8} \frac{(0.99951)\ (0.99924)}{(0.99940)^2} \exp\ (-0.029)$$

$$= (1.0045)\ (3.96)\ (1.00)\ (0.971)$$

$$= 3.98$$

It can be seen that the vibrational, translational and zero-point energies contribute in a minor way to the K_P of the reaction. The important term is the ratio of rotational partition functions and in this ratio the effect of symmetry number predominates. ■

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Chapter 8

Non-equilibrium Thermodynamics

The thermodynamics discussed so far is based on the concept of equilibrium and hence should be called *equilibrium thermodynamics*. As already discussed in Chapter 2, equilibrium is an idealized concept and can be attained only in infinite time. The other concept, which the equilibrium thermodynamics heavily relies upon is the concept of reversibility; reversible operations. Since every point on a reversible path is an equilibrium point, moving along a reversible path is moving from one equilibrium point to another and so on. The perfectly reversible path is nothing more than a concept and resides only in our imagination. Thus equilibrium thermodynamics is not the thermodynamics of real systems or real situations. Further, the equilibrium thermodynamics deals either with isolated systems or closed systems. Since the systems which nature has created, e.g. living system—plants or animals—are open systems, the equilibrium thermodynamics is incompetent to deal with them, because attainment of equilibrium is out of question in open systems. The time invariant situation attained in open systems is steady state and not equilibrium (refer to Chapter 2), thermodynamics having competence to deal with open systems can be given either of the following names: (i) thermodynamics of open system (ii) thermodynamics of steady state (iii) thermodynamics of irreversible processes (iv) non-equilibrium thermodynamics. Since the emergence of this new thermodynamics owes its origin to the reciprocal relations discovered by Onsager it is sometimes also called *Onsager's thermodynamics*. Onsager's reciprocal relations which in fact are at the very foundations of this new thermodynamics have been given the status of fourth law of the Thermodynamics.

Before the emergence of non-equilibrium thermodynamics as a tool there are several examples of treating non-equilibrium processes using the methods of equilibrium thermodynamics. The example which is most worthy of mention in this context is Thomson's treatment of thermoelectricity. The approach was to divide the whole process into reversible and irreversible parts and not to take into account the part essentially considered to be irreversible. Surprisingly, the results obtained by Thomson were completely confirmed by experiments. This certainly is an example where right results were obtained using wrong methods. The other example which merits mention here is Srivastava's treatment of thermal transpiration of a chemically dissociating gas, which clearly demonstrated that

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equilibrium methods were not capable of dealing with non-equilibrium process like thermal transpiration. Srivastava's treatment of thermal transpiration of a dissociating gas is summarized below.

8.1 SRIVASTAVA'S TREATMENT[1]

The phenomenon of thermal transpiration or thermomolecular pressure difference is the transport through a capillary or a network of capillaries under the influence of temperature difference. Consider a system consisting of two chambers of volumes V and V', maintained at temperatures T and T' respectively and which communicate through a porous diaphragm.

Suppose in the steady state, the molecular concentrations in the two chambers are n and n'. The equality of flux yields

$$\frac{1}{4}n\sqrt{\frac{8kT}{m\pi}} = \frac{1}{4}n'\sqrt{\frac{8kT'}{m\pi}},$$

where k being the Boltzmann constant. Then

$$n\sqrt{T} = n'\sqrt{T'} \tag{8.1}$$

Further

$$Vn + V'n' = \frac{M}{m} \tag{8.2}$$

where M is the total mass of the gas and m its molecular weight. From Equations (8.1) and (8.2), it follows that

$$n = \frac{M/m}{V + V'\sqrt{T/T'}}; \qquad n' = \frac{(M/m)\sqrt{T/T'}}{V + V'\sqrt{T/T'}} \tag{8.3}$$

Consider that the gas consists of the molecules of the type X_2 and some of it dissociates into atoms X. Each chamber will then contain X_2 molecules and X atoms which will have to be in equilibrium with each other and also in mechanical equilibrium with the other chamber. It will be seen that under these circumstances the concentrations n_1, n_2, n_1', n_2' (n_1 referring to atoms and n_2 to the molecules) cannot simultaneously satisfy the condition of chemical or thermodynamical equilibrium and also the condition that in the steady state the net flux is zero for each constituent. If both conditions were satisfied, we should have

$$n_1^2 = Kn_2, \qquad n_1'^2 = K'n_2' \tag{8.4, 8.5}$$

and

$$n_1\sqrt{T} = n_1'\sqrt{T'}, \qquad n_2\sqrt{T} = n_2'\sqrt{T'} \tag{8.6, 8.7}$$

1. Srivastava, B.N. *Proc. Roy. Soc., 175A*, 474 (1940).

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where K represents the equilibrium constant. From Equations (8.6) and (8.7), we get

$$\frac{n_1}{n_2} = \frac{n_1'}{n_2'} \tag{8.8}$$

and from Equations (8.4) and (8.5), we have

$$\frac{K}{K'} = \frac{n_1^2}{n_2}\frac{n_2'}{n_1'^2} = \frac{n_1}{n_1'} \qquad \text{from Equation (8.8)}$$

$$= \sqrt{\frac{T'}{T}} \qquad \text{from Equation (8.6)}$$

This evidently shows that both the above conditions can be satisfied only when K varies as $T^{-1/2}$. Experimentally and theoretically, we know that K generally varies exponentially with T and hence the condition $K/K' = \sqrt{(T'/T)}$ cannot be satisfied in practice. Therefore, Equations (8.4)–(8.7) cannot all hold true. Strictly speaking, it is, therefore, not a case of true thermodynamic equilibrium and the law of reaction isochore will not be obeyed. It is merely a case of steady state where the processes of chemical reaction and molecular effusion so balance each other that the atomic and molecular concentrations assume fixed values, which do not vary with time.

The message from Srivastavs's analysis, therefore, is that a new tool is needed to deal with such steady state processes. The methods based on equilibrium are inadequate. A really systematic macroscopic and general thermodynamics of 'irreversible processes' is based on a theory published[2] by Onsager in 1931 and later refined by Casimir. The proof of Onsager's theorem, which is based on general ideas of statistical mechanics will not be given in this book (the inquisitive reader may refer to the original papers cited in the footnote). One can, however, consider Onsager's theorem as a new principle of thermodynamics and accept it as an axiom.

8.2 BASIC POSTULATES AND METHODOLOGY

Before we take up basic postulates and methodology of irreversible thermodynamics let us recapitulate what an irreversible process is. We know from the second law that any process that would reduce the entropy of an isolated system is an impossible process. Suppose a process takes place within an isolated system in what we shall call the forward direction. If the entropy increases in the forward process, then for the backward process the entropy would decrease. The backward process, therefore, is impossible and the forward process is irreversible. For a reversible process the entropy should remain unchanged during the process.

Let us keep in mind that system plus environment can always be taken to be an isolated system. Thus we can write for the change in entropy of a system as

$$dS = d_eS + d_iS = \frac{dQ}{T} + d_iS \tag{8.9}$$

2. Onsager, *Phys. Rev.*, *37*, 405 (1931), *38*, 2265 (1931). Onsager got the Nobel Prize for this work.

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where d_eS and dQ are respectively the entropy and heat supplied to the system by its environment and d_iS is the entropy produced inside the system by irreversible processes. It is supposed that system is a so-called closed one, i.e. only having heat exchange with the surroundings but no exchange of matter. If the exchange of matter also takes place, the system is called an *open system* and d_eS contains another term representing the supply of entropy carried by the transfer of matter. The external supply of entropy, d_eS may be, zero or negative but the internal production of entropy d_iS is positive definite. Clausius called the quantity Td_iS as the, *non-compensated heat*, which did not become very popular. It is easy to see that, for reversible processes, when $d_iS = 0$,

$$dS = \frac{dQ}{T} \tag{8.10}$$

and for irreversible processes when $d_iS > 0$

$$dS > \frac{dQ}{T} \tag{8.11}$$

The quantity d_iS is relevant in the formalism of irreversible thermodynamics. We shall demonstrate its usefulness in the formalism of irreversible thermodynamics in a short while from now. In the mean time, let us introduce the phenomenological rate equations.

8.2.1 The Rate Laws

Non-equilibrium systems are different from equilibrium system, because in the latter there are no flows of matter or energy or both. Flows are caused by certain agencies, e.g. gradient of temperature, gradient of electrical potential, gradient of concentration, etc. These agencies have been given a general name 'driving forces' or 'forces' in the thermodynamics of irreversible processes. This name is sometimes misleading because these forces have nothing to do with the forces in the Newtonian sense. This is why some authors prefer the name 'affinities' to designate this class of quantities. The thermodynamic forces or affinities are symbolized by $X_i (i = 1, 2 \cdots)$. The irreversible phenomena caused by these forces, e.g. heat flow, electrical current, chemical reaction rate are called 'fluxes' or 'flows' or 'currents' and are usually symbolized by J_i $(i = 1, 2, \ldots)$. The normal expectation is that a temperature gradient would give rise only to heat flow and a concentration gradient would give rise only to mass flow. But we know that a temperature gradient and a concentration gradient could both cause mass flow (thermal diffusion and ordinary diffusion). The same two forces could also cause heat flows —ordinary heat conduction and the Dufour effect. In the most general case, we can write

$$J_i = J_i (X_1, X_2, \ldots) \tag{8.12}$$

If the system is not very far away from the equilibrium, i.e. the values of X_1, X_2 etc., are not very large, using Taylor's expansion and neglecting the square and higher order terms, we can write

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$$J_i = \sum_{j=1}^{n} \left(\frac{\partial J_1}{\partial X_j}\right)_0 X_j + \dots \tag{8.13}$$

The subscript '0' in the Equation (8.13) indicates that derivative is for close to equilibrium situation. So the irreversible phenomena can be expressed by linear phenomenological relations of the type

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \tag{8.14}$$

where

$$L_{ij} = \left(\frac{\partial J_i}{\partial X_j}\right)_0 \tag{8.15}$$

It was Lord Rayleigh who in his famous treatise on the theory of sound used a set of equations that explicitly expressed the linear dependence of all mechanical flows on all mechanical forces operating in a system. Onsager in 1931 extended this concept to include all thermodynamic flows and forces. For a system containing n flows and n forces the phenomenological equations can be written as

$$\left.\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + \cdots + L_{1n}X_n \\ J_2 &= L_{21}X_1 + L_{22}X_2 + \cdots + L_{2n}X_n \\ &\vdots \qquad \vdots \qquad \vdots \qquad\qquad \vdots \\ J_n &= L_{n1}X_1 + L_{n2}X_2 + \cdots + L_{nn}X_n \end{aligned}\right\} \tag{8.16}$$

The coefficients L_{11}, L_{12}, etc., are called 'phenomenological coefficients'. The evaluation of these coefficients is one of the major objectives in irreversible thermodynamics. The phenomenological Equations (8.14) or (8.16) can also be written in the inverted matrix form, i.e.

$$X_i = \sum_{j=1}^{n} R_{ij} J_j, \qquad i = 1, 2, \dots \tag{8.17}$$

The coefficients R_{ij} have the characteristics of generalized resistances or frictions while L_{ij} have the characteristics of generalized conductances or mobilities. The relationship between L_{ij} and R_{ij} is not hard to discover. To do this let us consider a simple situation of two fluxes and two forces. The phenomenological equations for this case can be written either in the form of Equation (8.14) or in the form of Equation (8.17), i.e. either in the form

$$J_1 = L_{11}X_1 + L_{12}X_2, \qquad J_2 = L_{21}X_1 + L_{22}X_2 \tag{8.18}$$

or in the form

$$X_1 = R_{11}J_1 + R_{12}J_2, \qquad X_2 = R_{21}J_1 + R_{22}J_2 \tag{8.19}$$

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Using simple algebra, one can write

$$R_{11} = \frac{L_{22}}{|L|}; \quad R_{12} = \frac{-L_{12}}{|L|}; \quad R_{21} = \frac{-L_{21}}{|L|}; \quad R_{22} = \frac{L_{11}}{|L|} \tag{8.20}$$

where

$$|L| = L_{11}L_{22} - L_{12}L_{21} \tag{8.21}$$

In general

$$R_{ij} = \frac{|L|_{ij}}{|L|} \tag{8.22}$$

where $|L|$ is the determinant of the matrix of the coefficients L_{ij} and $|L|_{ij}$ is the minor of the determinant corresponding to the term L_{ij}. In which form, whether in the form of Equations (8.14) or in the form of Equation (8.17), one should write the phenomenological equations is determined by the convenience of analysis and physical reality. It must be emphasized that the linear phenomenological relations hold only for sufficiently slow processes occurring when the system is not too far away from the state of equilibrium. Inspite of this limitation the range of phenomena covered by the phenomenological equations is very wide and many processes of physical, chemical and biological interest are included. In the phenomenological equations (8.14) and (8.17) the coefficients L_{ii}, L_{jj} or R_{ii}, R_{jj} represent the normal expected phenomena, e.g. heat flow induced by the temperature gradient, electrical current iduced by the electrical potential difference etc. and are called *straight coefficients* while the coefficient L_{ij}, L_{ji} or R_{ij}, R_{ji} represent the interaction between the two different kinds of flows and are called *cross coefficients*, e.g. mass flow induced by temperature gradient (thermal diffusion), flow of electricity induced by pressure difference (streaming current) etc.

Although the linear phenomenological Equations (8.14) and (8.17) adequately summarize the thermodynamic information about slow processes, their application presents considerable difficulties. Even in the simplest case where there are only two fluxes and two forces the number of coefficients to be determined are four which means four independent experiments are required. As the number of fluxes and forces increase, the number of coefficient to be determined also increases. For example, in a three flux, three force situation the total number of coefficients to be determined is nine. That is, nine independent experiments to be performed. This presents considerable experimental difficulties and also the difficulties of analysis. Onsager's theorem which was stated as early as 1931 and which plays a central role in the thermodynamics of irreversible processes, reduces the number of coefficients and also predicts correlations between different transport phenomena. Onsager's theorem states that the matrix of the phenomenological coefficients is symmetric provided a proper choice is made of fluxes and forces which means

$$L_{ij} = L_{ji}, \qquad R_{ij} = R_{ji} \tag{8.23, 8.24}$$

Equations (8.23) and (8.24) are called *Onsager's reciprocal relations*. Broadly speaking the proper choice of fluxes and forces means that the flows and forces

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$$f = f^{(0)} + f^{(1)} + f^{(2)} + \cdots \tag{8.29}$$

where $f^{(0)}$ is the equilibrium distribution and $f^{(1)}$, $f^{(2)}$, etc., are successive approximations. Strictly speaking, thermodynamic functions are defined only in thermostatic equilibrium, i.e. when $f = f^{(0)}$. Prigogine compared the results of the thermodynamical theory based on Equation (8.28) with those of the statistical theory of irreversible processes in gases based on Enskog–Chapman model. It was revealed that the kinetic theory with $f = f^{(0)} + f^{(1)}$ gives the same results as the results from thermodynamics of irreversible processes based on Equation (8.28), but with the inclusion of $f^{(2)}$ the results from thermodynamics and kinetics do not agree. Thus Gibbs equation is valid only up to first-order perturbations, i.e. not very far from equilibrium.

8.2.2 Theorem of Minimum Entropy Production

After having made the proper choice of fluxes and forces one can conveniently write the linear phenomenological relations and proceed to evaluate the phenomenological coefficients. All measurements of thermodynamic parameters in classical as well as in irreversible thermodynamics are made when the system has attained a time-invariant state. The time-invariant situation in open systems is steady state (see Chapter 2) and differs from equilibrium state in that in the equilibrium state entropy production is zero while in the steady state it is positive definite. If no restraints are imposed on a system and it is left to age it will ultimately attain a state of equilibrium. If, however, we impose a number of constant constraints on the system. For example, the forces $X_1, X_2, ..., X_k$ are fixed at constant values and other forces $X_{k+1}, X_{k+2}, ..., X_n$ are allowed to adjust freely, the system would ultimately attain a steady state (see Chapter 2). The steady state is caused by the balancing of incoming fluxes by the outgoing fluxes while in the equilibrium, fluxes cease to exist. Equilibrium states are characterized by the maximization of entropy at constant energy and volume. A parallel criterion for the evaluation of steady states was worked out by Prigogine and is contained in the theorem of minimum entropy production which goes after his name. According to Prigogine's theorem of minimum entropy production, the state of minimum entropy production is the same as the state of no net flux. To illustrate this theorem, let us consider a simple system in which there are only two flows and two forces. The entropy production and the phenomenological equations for such a case can be written as

$$\sigma = J_1 X_1 + J_2 X_2 \tag{8.30}$$

and

$$J_1 = L_{11} X_1 + L_{12} X_2 \tag{8.31}$$

$$J_2 = L_{21} X_1 + L_{22} X_2 \tag{8.32}$$

Introducing Equations (8.31) and (8.32) in Equation (8.30), we obtain

$$\sigma = L_{11} X_1^2 + (L_{12} + L_{21}) X_1 X_2 + L_{22} X_2^2 \tag{8.33}$$

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which in view of Onsager's relations (8.23) can be written as

$$\sigma = L_{11}X_1^2 + 2L_{21}X_1X_2 + L_{22}X_2^2 \tag{8.34}$$

Let us now impose the restriction that X_1 = constant and allow X_2 to adjust. Differentiating σ with respect to X_2 holding X_1 constant, we obtain

$$\left(\frac{\partial \sigma}{\partial X_2}\right)_{X_1} = 2\left(L_{21}X_1 + L_{22}X_2\right) = 2J_2 \tag{8.35}$$

Now according to the new condition for the steady state, if X_2 is unrestricted the conjugate flow must vanish. Therefore, Equation (8.35) becomes

$$\left(\frac{\partial \sigma}{\partial X_2}\right)_{X_1} = 0 \tag{8.36}$$

which indicates that the entropy production has an extreme value in the steady state. Since σ is positive definite, this extremum must be a minimum and the stationary state of the system is that state in which the entropy production assumes a minimal value consistent with the restraints imposed. If the constraints imposed were X_2 = constant and X_1 were allowed adjust the state of minimum entropy production would have been equivalent to $J_1 = 0$. Similarly if the phenomenological equations are written in the inverted matrix form (Equation 8.19) the theorem of minimum entropy production would lead to the two stationary states in which $X_1 = 0$ and $X_2 = 0$. These considerations can easily be extended to the general cases in which n fluxes and n forces are operating.

If out of the n thermodynamic forces, k forces, $X_1, X_2, \ldots X_k$, are held constant and the remaining X_{k+1}, X_{k+2}, etc., are allowed to adjust, the stationary state achieved is said to be of the order k. Thus stationary state of the zeroth order is simply thermostatic equilibrium and what we have discussed above is the stationary state of the first order. The stationary state is comprehensive than equilibrium state—the latter is only a subset of the former.

A clearer insight into the theorem of minimum entropy production can be had from geometrical considerations. Equation (8.34) when represented on the coordinate axes, x, y and z gives a parboloid with its vertex at $\sigma = 0$. This has been depicted in Figure 8.1.

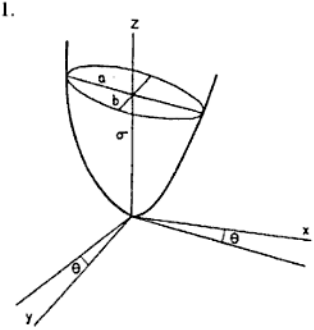

Figure 8.1 Entropy production in non-equilibrium state.

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The major and minor axes $2a$ and $2b$ respectively are inclined to the axes x and y at an angle θ given by

$$\theta = \frac{3\pi}{2} + \frac{1}{2}\tan^{-1}\left(\frac{2L_{12}}{L_{11} - L_{22}}\right) \tag{8.37}$$

Now let us suppose that the constraint X_2 (=constant) is imposed on the system. This means that the plane corresponding to X_2 (= constant) will cut the parboloid and the section would be a parabola given by the equation

$$\sigma = L_{11}X_1^2 + \beta X_1 + C \tag{8.38}$$

where $\beta = 2L_{21}X_2$ and $C = L_{22}X_2^2$. It is clear from the geometrical picture that the vertex of the parabola would correspond to the state of minimum entropy production, i.e. stationary state. By applying the usual methods of coordinate geometry, the coordinates of the vertex of the parabola are given by

$$\sigma = \frac{X_2^2\left(L_{11}L_{22} - L_{12}L_{21}\right)}{L_{11}} \tag{8.39}$$

and

$$X_1 = -\frac{L_{12}}{L_{11}}X_2 \tag{8.40}$$

The latus rectum of the parabola would be equal to $1/L_{11}$. The other parameters in the stationary state can be calculated without much difficulty and are given as follows:

$$J_2 = \frac{L_{11}L_{22} - L_{12}L_{21}}{L_{11}}X_2 \tag{8.41}$$

and

$$J_1 = 0 \tag{8.42}$$

Similar evaluation of the parameters in the stationary state when the constraint X_1 (=constant), is imposed on the system, can be done.

The conditions $J_1 = 0$ or $J_2 = 0$ in the stationary state represent the conditions of no net flux. These should not be confused with the situation where all flows cease to exist (thermostatic equilibrium). The phenomenological equations for J_1 or J_2 are composed of two terms, e.g.

$$J_1 = L_{11}X_1 + L_{12}X_2 = J_1' + J_1'' \tag{8.43}$$

J_1' is the flow induced by X_1 and J_1'' is the flow induced by X_2. In the stationary state, J_1' and J_1'' balance each other so that $J_1 = 0$. In the state of thermostatic equilibrium, both J_1' and J_1'' should be individually equal to zero.

8.2.3 Positive Definite Character of σ and Phenomenological Coefficients

The positive definite character of σ imposes a few restrictions on the values of the phenomenological coefficients. We know that for non-equilibrium state

$$\sigma = L_{11}X_1^2 + \left(L_{12} + L_{21}\right)X_1X_2 + L_{22}X_2^2 \tag{8.44}$$

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Since X_1 and X_2 can be individually made to vanish, Equation (8.44) leads to

$$L_{11}X_1^2 \geq 0, \qquad L_{22}X_2^2 \geq 0 \tag{8.45}$$

which implies that both coefficients L_{11} and L_{22} must be positive. Further, Equation (8.44) can be transformed into

$$\sigma = L_{11}\left[X_1 + \frac{L_{12} + L_{21}}{2}\frac{X_2}{L_{11}}\right]^2 + \left[L_{22} - \left(\frac{L_{12} + L_{21}}{2}\right)^2 \frac{1}{L_{11}}\right]X_2^2 \tag{8.46}$$

Since $\sigma > 0$, Equation (8.46) in view of the relationship (8.45) leads to

$$L_{22} - \left(\frac{L_{12} + L_{21}}{2}\right)^2 \frac{1}{L_{11}} > 0$$

or

$$\left(L_{21} + L_{12}\right)^2 < 4L_{11}L_{22} \tag{8.47}$$

The analysis given above clearly shows that L_{11} and L_{22} are always positive while cross-coefficients L_{12} and L_{21} may be positive or negative.

8.2.4 The Curie–Prigogine Principle

In phenomenological Equation (8.14) or (8.17) or (8.18) or (8.19), it is implied that linear coupling between all forces and all flows operating in the irreversible processes in the system is possible. But this assumption needs a more critical scrutiny, because it is an important question whether a coupling can exist between fluxes and forces of different tensorial orders. Consider an isothermal system with a scalar flow J_S and a conjugate scalar force X_S and a vectorial flux J_V and the corresponding vectorial force X_V. The entropy production in this case is given by the equation

$$T\sigma = J_S X_S + J_V X_V \tag{8.48}$$

The phenomenological relations for J_S and J_V can now be written as

$$J_S = L_{SS}X_S + L_{SV}X_V \tag{8.49}$$

$$J_V = L_{VS}X_S + L_{VV}X_V \tag{8.50}$$

From Equations (8.49) and (8.50), it follows that for an isotropic system the coefficients L_{SS}, L_{VV} should be scalars and the cross-coefficients L_{SV} and L_{VS} should be vectors. This is because in an isotropic system the reversal of sign of all the coordinate axes must leave the phenomenological coefficients invariant. L_{SS} being a scalar fulfils this requirement automatically. L_{VV} must also be a scalar in order that it remains invariant with the reversal of the coordinate system. The vectors L_{SV} and L_{VS} can remain invariant with the reversal of the coordinates only if both of them are individually equal to zero. This means there can be no coupling between scalar and vector quantities. This is the *Curie–Prigogine principle* and is of immense importance while dealing with the application of irreversible thermodynamics to biological systems, e.g. active transport etc. However, in

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anisotropic systems in the stationary state this restriction need not be valid and Equations (8.49) and (8.50) can be found useful.

The thermodynamics of irreversible processes is now summarized based on the following fundamental points:

1. In an irreversible process the entropy production σ is positive definite.
2. The entropy production σ can be expressed as the sum of the products of conjugate fluxes and forces, i.e.

$$\sigma = \frac{d_i S}{dt} = \sum_i^n J_i X_i \tag{8.25}$$

which in turn can be utilized to choose appropriate fluxes and forces.

3. The rate equations are expressed in the form of linear phenomenological equations, i.e.

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \tag{8.14}$$

or

$$X_i = \sum_{j=1}^{n} R_{ij} J_j \tag{8.17}$$

4. The matrix of the phenomenological coefficients L_{ij} is symmetric provided a proper choice of fluxes and forces is made, i.e.

$$L_{ij} = L_{ji} \tag{8.23}$$

$$R_{ij} = R_{ji} \tag{8.24}$$

5. The Gibbs entropy equation, i.e. Equation (8.28) is valid even outside equilibrium—up to first order perturbations. The Gibbs equation with the help of laws of energy conservation and mass conservation can be transformed into the form of Equation (8.25).

   The domain of validity of the Gibbs equation is larger than the domain of validity of linear laws (Equations 8.14 and 8.17) and Onsager's relations (Equations 8.23 and 8.24).

6. The state of no net flux in the steady state is the state of minimum entropy production.

The procedure followed in the application theory is simple. For the identified system, Gibbs entropy equation is written. The Gibbs equation is then transformed into the form of Equation (8.25) using laws of conservation of mass and energy, from which appropriate fluxes and forces are chosen. The linear phenomenological equations are then written from which the expressions for the various effects in the steady state are derived; the theorem of minimum entropy production is utilized to evaluate the values of the parameters in the steady states. The Onsager's reciprocal relations serve the useful purpose of reducing the number of

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phenomenological coefficient and also in discovering the interrelationships between the different steady state effects. The values of the various phenomenological coefficients which represent the various steady state effects are evaluated experimentally or otherwise and are interpreted in terms of the mechanism of the phenomenon.

We will now take up a few examples illustrated in the next sections.

8.3 EXAMPLES OF NON-EQUILIBRIUM THERMODYNAMICS

8.3.1 Thermoelectricity

The first theory of thermoelectricity was given in 1854 by Lord Kelvin. His theory may be classified among the pseudo thermostatic theories. We shall now give the thermodynamical theory based linear phenomenological laws and Onsager's relations.

Let us suppose that we have a thermocouple made of two metals A and B with junctions at temperatures T and $(T + \Delta T)$ in two heat reservoirs 1 and 2. In the wire A a condenser 3 is inserted. The system is schematically depicted in Figure 8.2.

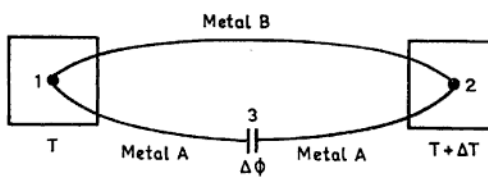

Figure 8.2 Thermocouple.

A potential difference $\Delta\phi$ is generated over the condenser. Let us suppose that the condenser has no heat capacity. Let us also suppose that the wires A and B are at every point in contact with a heat reservoir of large heat capacity with the same temperature as the wire at the point of contact. Then the change of entropy in the total system is simply the sum of the changes of entropy in the reservoirs and in the condenser. For each of these parts we can write using Gibbs equation that

$$T\,dS = dU - \phi\,de \tag{8.51}$$

where T is the temperature, S the entropy, U the energy, ϕ the electrical potential and e the charge of the subsystem. When an amount of energy dU is carried from reservoir 1 to reservoir 2 and a charge de is brought on the condenser, the change of entropy of the total system is

$$dS = dS_1 + dS_2 + dS_3 = \frac{-dU}{T} + \frac{dU}{T+\Delta T} - \frac{\Delta\phi\,de}{T} \tag{8.52}$$

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$$T\,dS^{\mathrm{I}} = dU^{\mathrm{I}} + P^{\mathrm{I}}dV^{\mathrm{I}} - \sum_{k=1}^{n} \mu_k^{\mathrm{I}}\, dM_k^{\mathrm{I}} \tag{8.65}$$

and

$$T\,dS^{\mathrm{II}} = dU^{\mathrm{II}} + P^{\mathrm{II}}dV^{\mathrm{II}} - \sum_{k=1}^{n} \mu_k^{\mathrm{II}}\, dM_k^{\mathrm{II}} \tag{8.66}$$

respectively. Using Equations (8.61) to (8.66), the Gibbs entropy equation for the total system (I + II) can be written as

$$T\,dS = T\,dS^{\mathrm{I}} = T\,dS^{\mathrm{II}}$$

or

$$T\,dS = dQ - \sum_{k=1}^{n} \left(\mu_k^{\mathrm{I}} + e_k\phi^{\mathrm{I}} - \mu_k^{\mathrm{II}} - e_k\phi^{\mathrm{II}}\right) dM_k^{\mathrm{I}} \tag{8.67}$$

Comparing Equation (8.67) with the equation

$$dS = d_eS + d_iS \tag{8.68}$$

where d_eS and d_iS are the entropy change due to the exchange of heat with the surrounding and entropy change due to the irreversible processes going on in the system respectively, we can write

$$d_eS = \frac{dQ}{T} \tag{8.69}$$

and

$$d_iS = -\sum \Delta\left(\mu_k + e_k\phi\right)\frac{dM_k^{\mathrm{I}}}{T} \tag{8.70}$$

In Equation (8.70), Δ represents the difference of the quantities between the subsystems I and II. Realizing that for the system under consideration

$$\Delta\mu_k = v_k\Delta P \tag{8.71}$$

where v_k is the partial specific volume of the component k we can deduce from Equation (8.70) that

$$T\sigma = \frac{Td_iS}{dt} = -\sum_k v_k \frac{dM_k^{\mathrm{I}}}{dt}\Delta P - \sum_k e_k \frac{dM_k^{\mathrm{I}}}{dt}\Delta\phi \tag{8.72}$$

Equation (8.72) can be rewritten in the form

$$T = J_V\Delta P + I\Delta\phi \tag{8.73}$$

where I is given by Equation (8.64) and the volume flux J_V is given by equation

$$J_V = \sum_{k=1}^{n} v_k \frac{dM_k^{\mathrm{I}}}{dt} \tag{8.74}$$

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It is now obvious from Equation (8.73) that appropriate pairs of fluxes and forces are J_V and ΔP and I and $\Delta\phi$. Since T is held constant, the linear phenomenological equations can now be written as

$$I = L_{11}\Delta\phi + L_{12}\Delta P \tag{8.75}$$

$$J_V = L_{21}\Delta\phi + L_{22}\Delta P \tag{8.76}$$

or alternatively as

$$\Delta\phi = R_{11}I + R_{12}J_V \tag{8.77}$$

$$\Delta P = R_{21}I + R_{22}J_V \tag{8.78}$$

It should be easy to see that application of the theorem of minimum entropy production would yield the following steady states

$$I = 0, \quad \Delta P = 0, \quad J_V = 0, \quad \Delta\phi = 0 \tag{8.79}$$

The expression for the corresponding steady state effects can be written, using the linear phenomenological equations, as follows:

For streaming potential

$$\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = -\frac{L_{12}}{L_{11}} \tag{8.80}$$

For electro-osmosis

$$\left(\frac{J_V}{I}\right)_{\Delta P=0} = \frac{L_{21}}{L_{11}} \tag{8.81}$$

For electro-osmotic pressure difference

$$\left(\frac{\Delta P}{\Delta\phi}\right)_{J_V=0} = -\frac{L_{21}}{L_{22}} \tag{8.82}$$

For streaming current

$$\left(\frac{I}{J_V}\right)_{\Delta\phi=0} = \frac{L_{12}}{L_{22}} \tag{8.83}$$

In view of the Onsager's relations, the following interrelationships automatically follow, i.e.

$$\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = -\left(\frac{J_V}{I}\right)_{\Delta P=0} \tag{8.84}$$

and

$$\left(\frac{\Delta P}{\Delta\phi}\right)_{J_V=0} = -\left(\frac{I}{J_V}\right)_{\Delta\phi=0} \tag{8.85}$$

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$$\Phi = T\sigma = \sum_{i=1}^{n} J_i \text{ grad } (-\mu_i) \tag{8.92}$$

The function Φ is called *dissipation function*.[7] For the sake of simplification let us consider that the discontinuous system is in the state of stationary flow, i.e. flows are constant. To evaluate the dissipation per unit area of the membrane as a whole let us integrate Equation (8.92) across the membrane.

$$\int_0^{\Delta x} \phi dx = \Phi = \int_0^{\Delta x} \sum_{i=1}^{n} J_i \text{grad } (-\mu_i) = \sum_{i=1}^{n} J_i \int_0^{\Delta x} -\frac{d\mu_i}{dx} dx \tag{8.93}$$

$$= \sum_{i=1}^{n} J_i \left(\mu_i^0 - \mu_i^{\Delta x}\right)$$

where the superscripts 0 and Δx represent that the values are for the surface at $x = 0$ and $x = \Delta x$, respectively. Rewriting Equation (8.93), we get

$$\Phi = \sum_{i=1}^{n} J_i \Delta\mu_i \tag{8.94}$$

In deriving Equation (8.94), the flows have been considered along the x coordinate, i.e. perpendicular to the membrane. μ_i^0 and $\mu_i^{\Delta x}$ in Equations (8.93) refer to the values of μ_i in the membrane phase at $x = 0$ and $x = \Delta x$. In order that chemical potentials μ_i in Equations (8.93) or (8.94) become accessible to experimental determination Kirkwood's suggestion is invoked. It is assumed that μ_i^0 (membrane) = μ_i^0 (adjacent solution) and $\mu_i^{\Delta x}$ (membrane) = $\mu_i^{\Delta x}$ (adjacent solution). Thus $\Delta\mu_i$ is equal to the difference in chemical potential of the ith component in the left- and right-hand compartments. Clarity about Kirkwood's suggestion can be obtained by considering a thin transition layer of thickness dx between the membrane surface and the adjacent solution—the layer being partially in the solution and partially in the membrane. The chemical potential of the i^{th} component at the point x in the solution is μ_i^x, while its value at the point $x + dx$ in the membrane is μ_i^{x+dx}. Expanding μ_i^{x+dx} in Taylor series and retaining only the first term, we get

$$\mu_i^{x+dx} = \mu_i^x + \frac{d\mu_i}{dx} dx \tag{8.95}$$

As $dx \to 0$, $\mu_i^{x+dx} \to \mu_i^x$ unless $d\mu_i/dx$ is infinite which is impossible. Thus the chemical potential will be the same on both sides of the boundary. It must be clarified that continuity of chemical potentials across the dividing surface does not imply continuity of the thermodynamic forces, $d\mu_i/dx$ at the surface. Figure 8.5 illustrates this point in the simple case of a stationary flux of a single permeance across the boundary between two phases.

7. It is often convenient to use instead of σ the function $\Phi = T\sigma$ which was called by Lord Rayleigh the dissipation function particularly in isothermal processes.

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Expanding $\ln\left(1 - x_s^0\right)$ and $\ln\left(1 - x_s^{\Delta x}\right)$ and neglecting the square and higher-order terms, we can rewrite Equation (8.100) as

$$\Delta\mu_w = \bar{V}_w \Delta P + RT\left(x_s^0 - x_s^{\Delta x}\right) \tag{8.101}$$

We know that the osmotic pressure Π is given by the equation

$$\Pi = C_s RT = \frac{n_s}{V} RT \tag{8.102}$$

Since

$$V = n_w \bar{V}_w + n_s \bar{V}_s \approx n_w \bar{V}_w \tag{8.103}$$

for a dilute solution and

$$x_s = \frac{n_s}{n_w + n_s} \approx \frac{n_s}{n_w} \tag{8.104}$$

Equation (8.102) can be rewritten as

$$\Pi = \frac{x_s}{\bar{V}_w} RT \tag{8.105}$$

In Equations (8.102) to (8.105), n represents the number of moles of the component represented by the subscripts. Using Equation (8.105), Equation (8.101) for $\Delta\mu_w$ can be written as

$$\Delta\mu_w = \bar{V}_w \Delta P - \bar{V}_w\left(\Pi^0 - \Pi^{\Delta x}\right)$$

or

$$\Delta\mu_w = \bar{V}_w\left(\Delta P - \Delta\Pi\right) \tag{8.106}$$

Similarly to transform $\Delta\mu_s$ in terms of experimentally measurable quantities ΔP and $\Delta\Pi$, we start with equation

$$\mu_s = \mu_s\left(T, P, x_s\right) \tag{8.107}$$

x_s being the mole fraction of the solute.

Proceeding in the same manner as shown above, we can write

$$\Delta\mu_s = \bar{V}_s \Delta P + RT \ln \frac{x_s^0}{x_s^{\Delta x}} \tag{8.108}$$

Using the expansion

$$\ln Y = 2\frac{Y - 1}{Y + 1} + \frac{1}{3}\left(\frac{Y - 1}{Y + 1}\right)^3 + \cdots \tag{8.109}$$

and retaining only the first-order terms, Equation (8.108) can be transformed into

$$\Delta\mu_s = \bar{V}_s \Delta P + RT \frac{x_s^0 - x_s^{\Delta x}}{\bar{x}_s} \tag{8.110}$$

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where $\bar{x}_s$ is the average value given by the equation

$$\bar{x}_s = \frac{x_s^0 + x_s^{\Delta x}}{2} \tag{8.111}$$

Using Equations (8.103) and (8.104), Equation (8.111) for dilute solutions can be transformed into

$$\bar{x}_s = \bar{V}_w \bar{c}_s \tag{8.112}$$

In view of Equations (8.112) and (8.105), from Equation (8.110), we can write that

$$\Delta\mu_s = \bar{V}_s \Delta P + \frac{\Delta\Pi}{\bar{c}_s} \tag{8.113}$$

Introducing explicit expressions for $\Delta\mu_w$ and $\Delta\mu_s$ from Equations (8.106) and (8.113) into Equation (8.96) and rearranging the terms, we get

$$\Phi = \left(J_w \bar{V}_w + J_s \bar{V}_s\right)\Delta P + \left(\frac{J_s}{\bar{c}_s} - J_w \bar{V}_w\right)\Delta\Pi \tag{8.114}$$

or

$$\Phi = J_v \Delta P + J_D \Delta\Pi \tag{8.115}$$

where,

$$J_v = J_w \bar{V}_w + J_s \bar{V}_s \tag{8.116}$$

and

$$J_D = \frac{J_s}{\bar{c}_s} - J_w \bar{V}_w \tag{8.117}$$

J_v is the total volume flow across the membrane. Since the average volume fraction of water in the two compartments, $c_w \bar{V}_w$, is very close to unity so that $\bar{V}_w = 1/\bar{c}_w$ and J_s and J_w are respectively equal to $\bar{c}_s v_s$ and $\bar{c}_w v_w$, where v_s and v_w are the velocities of the centre of mass of the components denoted by the subscripts, we have from Equations (8.116) and (8.117)

$$J_v = J_w \bar{V}_w + J_s \bar{V}_s = c_w \bar{V}_w v_w + c_s \bar{V}_s v_s \tag{8.118}$$

and

$$J_D = \frac{J_s}{\bar{c}_s} - J_w \bar{V}_w \equiv \frac{J_s}{\bar{c}_s} - \frac{J_w}{\bar{c}_w} = \frac{\bar{c}_s v_s}{\bar{c}_s} - \frac{\bar{c}_w v_w}{\bar{c}_w} \tag{8.119}$$

or

$$J_D \equiv v_s - v_w$$

Thus it is obvious from Equation (8.119) that J_D is velocity of the solute relative to that of the solvent. Since $\bar{C}_w \bar{V}_w >> \bar{C}_s \bar{V}_s$ and $\bar{C}_w \bar{V}_w \approx 1$, we have from Equation (8.118)

$$J_v \approx v_w \tag{8.120}$$

Thus the volume flow J_v may be regarded as the external velocity of the solvent, v_w. Now picking up fluxes and from Equation (8.115) the linear phenomenological equations can be written as

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$$\left(\frac{J_D}{\Delta P}\right)_{\Delta\Pi=0} = \left(\frac{J_v}{\Delta\Pi}\right)_{\Delta P=0} \tag{8.131}$$

Now let us consider the measurement of osmotic pressure with a membrane. The arrangement is schematically shown in Figure. 8.6. It is common knowledge that volume flows through the membrane will take place from lower-concentration side to the higher-concentration side and a pressure difference (ΔP) will start building up, which ultimately will become invariant with time.

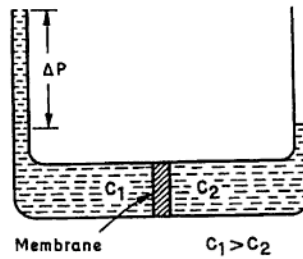

Figure 8.6 Schematic depiction of an osmometric arrangement.

The steady value of ΔP is taken to be equal to the osmotic pressure difference $\Delta\Pi$, i.e.

$$\Delta P = \Delta\Pi \tag{8.132}$$

When time invariant situation is reached the osmotically induced volume flow is balanced by the hydrostatically driven volume flow in the opposite direction so that the net volume flow J_v vanishes. From Equation (8.121) it follows, therefore, that in the steady state,

$$L_{11}\Delta P = -L_{12}\Delta\Pi$$

or

$$\left(\frac{\Delta P}{\Delta\Pi}\right)_{J_v=0} = -\frac{L_{12}}{L_{11}} = \sigma \text{ (say)} \tag{8.133}$$

It is obvious from Equation (8.133) that the steady value of pressure difference observed in the osmometer will be equal to $\Delta\Pi$ only when $\sigma = 1$, and when $\sigma < 1$, $\Delta P < \Delta\Pi$. This fact was first recognized by Stavermann who called σ as reflection coefficient, the value of σ ranges between zero and one. The perfectly semi-permeable membrane corresponds to $\sigma = 1$ and $\sigma = 0$ corresponds to perfectly leaky membrane, i.e. which is equally open (permeable) to both solute and solvent. When $\sigma = 1$, the solute is totally reflected back from the membrane and when $\sigma = 0$, all the solute passes through the membrane. This probably is the genesis of the name reflection coefficient. To appreciate further the concept of reflection coefficient let us write from Equations (8.121) and (8.122) the following equation, i.e.

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$$\left(\frac{J_D}{J_v}\right)_{\Delta\Pi=0} = \frac{L_{21}}{L_{11}} = \frac{L_{12}}{L_{11}} = -\sigma \tag{8.134}$$

Introducing the values of J_D and J_v in terms of velocities in Equation (8.134), we get

$$\left(\frac{v_s - v_w}{v_w}\right)_{\Delta\Pi=0} = -\sigma$$

or

$$\left(\frac{v_s}{v_w}\right)_{\Delta\Pi=0} = 1-\sigma \tag{8.135}$$

Equation (8.135) reveals that when $\sigma = 1$ (ideal semi-permeable membrane) $v_s = 0$, i.e. no solute passes through the membrane and when $\sigma = 0$, i.e. solute and solvent move with equal velocities through the membrane.

Using Equations (8.116) and (8.117), we can write

$$J_D + J_v = \frac{J_s}{\bar{c}_s} - J_w\bar{V}_w + J_w\bar{V}_w + J_s\bar{V}_s = \frac{J_s}{\bar{c}_s} + J_s\bar{V}_s = \frac{J}{\bar{c}_s}\left(1 + \bar{c}_s\bar{V}_s\right) \tag{8.136}$$

Since $\bar{c}_s\bar{V}_s << 1$ for dilute solution, Equation (8.136) reduces to

$$J_D + J_v = \frac{J_s}{\bar{c}_s} \tag{8.137}$$

Now using Equations (8.121) and (8.122), we can write from Equation (8.137) that

$$\frac{J_s}{\bar{c}_s} = \left(L_{11} + L_{21}\right)\Delta P + \left(L_{12} + L_{22}\right)\Delta\Pi \tag{8.138}$$

The concept of semipermeability requires that $J_s = 0$ for all values of ΔP and $\Delta\Pi$ which in the light of Equation (8.138) means that for an ideal semi-permeable membrane,

$$-L_{12} = L_{11} = L_{22} \tag{8.139}$$

The phenomenological Equations (8.121) and (8.122) have been further transformed to suit the convenience of experimenters. Introducing σ into Equation (8.121), we have

$$J_v = L_{11}\left(\Delta P - \sigma\Delta\Pi\right) \tag{8.140}$$

Solving Equation (8.121) for ΔP, we get

$$\Delta P = \frac{J_v - L_{12}\Delta\Pi}{L_{11}} \tag{8.141}$$

Substituting from Equation (8.141), the value of ΔP in Equation (8.138) and using Equation (8.133) and rearranging terms, we get

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$$J_s = J_v(1 - \sigma)\bar{c}_s + \omega\Delta\Pi \tag{8.142}$$

where

$$\omega = \frac{\bar{c}_s\left(L_{11}L_{22} - L_{12}^2\right)}{L_{11}} \tag{8.143}$$

The new coefficient ω is called the *solute permeability coefficient* and is defined as

$$\omega = \left(\frac{J_s}{\Delta\Pi}\right)_{J_v=0} \tag{8.144}$$

For an ideal semipermeable membrane obeying Equation (8.139) it follows from Equation (8.143) that $\omega = 0$. For a perfectly leaky membrane $\sigma = 0$, i.e. $L_{12} = 0$.

The set of coefficients L_{11}, σ and ω are more convenient for the characterization of any membrane system, natural or man-made and have been widely used by several workers most notably by Katchalsky, Ginzburg and Dainty. The advantage of using Equation (8.140) is that the values of L_{11} and σ can be evaluated from a single experiment. One has to measure the values of J_v induced by ΔP in the presence of a fixed value of $\Delta\Pi$. To evaluate ω one has to measure solute flux induced by osmotic pressure difference when the condition $J_v = 0$ is imposed on the system. However, one word of caution should be recorded here. Any one using Equations (8.140) and (8.142) should first ascertain the validity of Onsager's relations as these are implied in the treatment.

8.3.4 Chemical Reactions

Let us consider a simple reaction going on at constant temperature and pressure

$$A \rightleftharpoons B$$

The Gibbs equation for the reaction can be written as

$$T\,dS = dU + P\,dV - \mu_A\,dM_A - \mu_B\,dM_B \tag{8.145}$$

Because of the law of conservation of mass, i.e.

$$dM_A + dM_B = 0$$

the Gibbs equation can be transformed into

$$T\,dS = dU + P\,dV - \left(\mu_A - \mu_B\right)dM_A \tag{8.146}$$

Splitting the change in entropy into two parts, i.e.

$$dS = d_eS + d_iS$$

it is clear from Equation (8.146) that

$$d_eS = \frac{dU + P\,dV}{T} = \frac{dQ}{T} \tag{8.147}$$

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and

$$d_i S = -\frac{(\mu_A - \mu_B) dM_A}{T} \tag{8.148}$$

Since affinity (A_1) of the chemical reaction is given by

$$A_1 = \mu_A - \mu_B$$

the equation for entropy production σ can be written from Equation (8.148) as

$$T_\sigma = J_1 A_1 \tag{8.149}$$

where the reaction rate

$$J_1 = -\frac{dM_A}{dt} \tag{8.150}$$

Equation (8.149) can be generalized to yield

$$T\sigma = \sum_{k=1}^{n} J_i A_i \tag{8.151}$$

Let us consider the two reactions between three substances A, B and C:

$$A \rightleftharpoons B \quad \text{and} \quad B \rightleftharpoons C \tag{8.152}$$

For the affinities of the two reactions, we have

$$A_1 = \mu_A - \mu_B; \quad A_2 = \mu_B - \mu_C \tag{8.153}$$

The phenomenological relations can be written as

$$J_1 = L_{11} A_1 + L_{12} A_2 \quad \text{and} \quad J_2 = L_{21} A_1 + L_{22} A_2$$

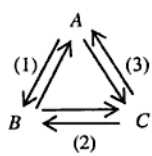
In the usual chemical kinetic treatment (as we will see a little later) the reactions (8.152) are independent, i.e.

$$L_{12} = L_{21} = 0 \tag{8.154}$$

and at the equilibrium state, we will have

$$J_1 = 0, \quad J_2 = 0 \quad \text{or} \quad A_1 = 0, \quad A_2 = 0 \tag{8.155}$$

More interesting than this is the case when a triangular reaction takes place between A, B and C, i.e.



For the present case of triangular monomolecular reaction we have three reaction rates J_1, J_2 and J_3 for the three reactions (1), (2) and (3) and three affinities A_1, A_2 and A_3 but these are not independent. We have for affinities

$$A_1 = \mu_A - \mu_B; \quad A_2 = \mu_B - \mu_C; \quad A_3 = \mu_C - \mu_A \tag{8.156}$$

It is now clear that

$$A_1 + A_2 + A_3 = 0 \tag{8.157}$$

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It is also obvious that

$$x_A + x_B = x_A^0 + x_B^0 = 1 \tag{8.178}$$

and

$$\alpha_A + \alpha_B = 0 \tag{8.179}$$

Using Equations (8.175) and (8.176), Equation (8.172) can be transformed into

$$J_1 = k_1\left(\alpha_A + x_A^0\right) - k_1'\left(\alpha_B + x_B^0\right) \tag{8.180}$$

Using Equations (8.174) to (8.176) and Equations (8.178) and (8.179), Equation (8.180) can be transformed to read

$$J_1 = \alpha_A\left(k_1 + k_1'\right) = k_1\alpha_A(1 + K) \tag{8.181}$$

Now let us write the affinity A_1 for the reaction in terms of α. We know that

$$A_1 = \mu_A - \mu_B$$

or

$$A_1 = \mu_A^0 + RT \ln x_A^0 + RT \ln\left(1 + \frac{\alpha_A}{x_A^0}\right) - \mu_B^0$$

$$- RT \ln x_B^0 - RT \ln\left(1 + \frac{\alpha_B}{x_B^0}\right) \tag{8.182}$$

In writing Equation (8.182), Equations (8.175) and (8.176) have been utilized. Since

$$\mu_A^0 + RT \ln x_A^0 = \mu_A\,(\text{equilibrium}) = \mu_B\,(\text{equilibrium}) = \mu_B^0 + RT \ln x_B^0 \tag{8.183}$$

Equation (8.182) reduces to

$$A_1 = RT\left[\ln\left(1 + \frac{\alpha_A}{x_A^0}\right) - \ln\left(1 + \frac{\alpha_B}{x_B^0}\right)\right] \tag{8.184}$$

The logarithmic terms in Equation (8.184) can be expanded in a power series from which second- and higher-order terms can be neglected in view of inequalities (8.177). Thus Equation (8.184) simplifies to the equation

$$A_1 = RT\left(\frac{\alpha_A}{x_A^0} - \frac{\alpha_B}{x_B^0}\right) = RT\,\frac{\alpha_A}{x_A^0}(1 + K) \tag{8.185}$$

Introducing Equation (8.185) in Equation (8.181), we get

$$J_1 = \frac{k_1 x_A^0}{RT} A_1 \tag{8.186}$$

Proceeding exactly in the same manner we can write for the reaction $C \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} D$ that

$$J_2 = \frac{k_2 x_r^0}{RT} A_2 \tag{8.187}$$

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where A_2 is the affinity of the reaction $C \rightleftharpoons D$. Now using Equations (8.167), (8.186) and (8.187), we can write for the chemical reaction system (8.166)

$$J_1' = \frac{1}{4}\left(k_1 x_A^0 + k_2 x_c^0\right)\frac{A_1'}{RT} + \frac{1}{4}\left(k_1 x_A^0 - k_2 x_c^0\right)\frac{A_2'}{RT} \tag{8.188}$$

$$J_2' = \frac{1}{4}\left(k_1 x_A^0 - k_2 x_c^0\right)\frac{A_1'}{RT} + \frac{1}{4}\left(k_1 x_A^0 + k_2 x_c^0\right)\frac{A_2'}{RT} \tag{8.189}$$

which have the same from as Equations (8.170) and (8.171) with

$$L_{11} = \frac{1}{4}\frac{k_1 x_A^0 + k_2 x_c^0}{RT} \tag{8.190a}$$

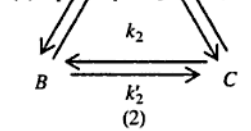
$$L_{12} = \frac{1}{4}\frac{k_1 x_A^0 - k_2 x_c^0}{RT} \tag{8.190b}$$

$$L_{21} = \frac{1}{4}\frac{k_1 x_A^0 - k_2 x_c^0}{RT} \tag{8.190c}$$

$$L_{22} = \frac{1}{4}\frac{k_1 x_A^0 + k_2 x_c^0}{RT} \tag{8.190d}$$

The validity of Onsager's reciprocal relations is obvious from Equations (8.190a)–(8.190d).

Now let us take up the case of monomolecular triangular reactions between A, B and C as shown below:



The reaction rates J_1, J_2 and J_3, respectively for the steps (1), (2) and (3) of the triangular reaction scheme are given by Equation (8.186) and the equations

$$J_2 = \frac{k_2 x_B^0}{RT} A_2; \quad J_3 = \frac{k_3 x_c^0}{RT} A_3 \tag{8.191}$$

where A_1, A_2 and A_3 are given by Equation (8.156) and are related to each other by Equation (8.157). Thus, we can write

$$J_1 - J_3 = \left(k_1 x_A^0 + k_3 x_c^0\right)\frac{A_1}{RT} + k_3 x_c^0 \frac{A_2}{RT} \tag{8.192}$$

$$J_1 - J_3 = k_3 x_c^0 \frac{A_1}{RT} + \left(k_2 x_B^0 + k_3 x_c^0\right)\frac{A_2}{RT} \tag{8.193}$$

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Onsager recognized that the principle of detailed balancing is a special case of the principle of microscopic reversibility formulated by Tolman as follows: "Under equilibrium condition any molecular process and the reverse of that process will be taking place on the average at the same rate. We may expect on the average, for a system at equilibrium the same frequency of transition from the condition, say, κ to ν as from ν to κ".

The fact that Onsager's reciprocal relations automatically follow from the kinetic treatment is a consequence of the implicit use of the principle of detailed balancing (Equations 8.195) in the derivation of the rate equations (for example, Equations (8.186), (8.187), (8.191), etc).

8.4 APPLICATIONS TO BIOLOGY

Since living organism (from both animal and plant kingdom) are open systems, non-equilibrium thermodynamics which deals with open systems is the right tool for their treatment. In this brief section it is neither feasible nor desirable to give a detailed account but, nevertheless, a couple of illustrative examples demonstrating the power of non-equilibrium thermodynamics as a tool for the treatment of living systems will be taken up. For a complete account, the readers are referred to the excellent monograph by Katchalsky and Curran.[8]

Entropy production

In general, we know that

$$\Phi = T\sigma = \sum_i J_i X_i \geq 0 \tag{8.196}$$

the equality holding at equilibrium and the inequality in the non-equilibrium state. The summation in Equation (8.196) does not require that each term individually be positive but that their sum be positive. Should any individual term J_iX_i be negative then the ith flow would proceed in a direction opposite to its thermodynamic force reducing the entropy production of the system. Such a term may be used within the cell system for organizational purposes. This is an important concept stemming the tide of entropic evolution yet in no way violating the second law. For example, the synthesis of ribonucleic acids involving the organization of constituent aminoacids is an entropy reducing process and depends upon the degree of coupling with metabolic reactions which provide sufficient entropy production for the overall dissipation function to be positive, i.e.

$$\Phi = J_{\text{synthesis}} A_{\text{synthesis}} + J_{\text{metabolism}} A_{\text{metabolism}} \geq 0 \tag{8.197}$$

The first term on the right-hand side in Equation (8.197) is negative and the second term is sufficiently positive to make overall $\Phi > 0$. We have already shown

8. Katchalsky, A. and Curran, P.F., *Non-equilibrium Thermodynamics in Biophysics*, Harvard University Press, Mass., 1967.

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that steady state is the state of minimum entropy production. The principle of minimum entropy production is valid only when the phenomenological coefficients are constants and do not vary with the thermodynamic forces; the Onsager's relation hold and the phenomenological relations are linear. The stationary state has the property of stability, since fluctuations from it generate forces which bring the system back to its original state. Any reduction in the number of restraints will cause reduction in entropy production of the stationary state so that ultimate state of equilibrium is achieved in an aged system under zero restraints and in which the entropy production vanishes. Prigogine and Wiame have applied this principle to the biological host. Maturity corresponds to a steady state compatible with external restraints, such as availability of food, temperature and other variables of the surroundings. The stationary state is also most economical since it corresponds to a minimal loss of free energy from the host. Thus the principle of minimum entropy production in the context of living systems implies that every organism tends to a state of maximum economy in metabolism.

Application to biological membrane system

We will now take up in brief discussion on the application of non-equilibrium thermodynamics to transport processes through biological membranes—particularly the phenomenon of active transport.

Biological membranes are complex in structure and selective in their function. In the thermodynamic analysis, the membrane is considered as a black box and one can try to deduce its transport mechanism and function from observation of input and output data. The position is like that of an industrial spy, who is not allowed to enter a factory and, therefore, tries to deduce the organization and functioning of the factory from examination of the raw material entering the factory and the finished products coming out of the factory. His conclusions would obviously be of a rather general nature. The conclusions drawn from non-equilibrium thermodynamic treatment are of similar nature. If someone wants to have information about the molecular mechanism of the transport processes he or she has to make use of other branches, e.g. kinetic theory, and interpret the phenomenological coefficients in terms of events at the molecular level.

Transport across biological membranes can be put in two broad categories—*passive transport* and *active transport*. Active transport is considered more important in the biological context. Mass transport induced by chemical potential difference/gradient, heat flow induced by temperature difference or gradient are some of the common examples of passive transport. The treatment of membrane transport processes (electrokinetic effects, osmosis, etc.) considered earlier in this package are all examples of passive transport. In passive transport, the flow is always from a higher potential to a lower potential. The striking point of difference in active transport is that the flow may be against the gradient of its conjugated force. The energy for driving such flows comes form some biological activity. Hence the name active transport. The biological activity is usually some internal metabolic enzymic reaction. Thus in essence, in active transport processes, diffusion process is coupled with a chemical (metabolic) reaction. Since diffusive

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flow is vectorial in character and the chemical affinity (of metabolic reaction) is scalar no coupling between diffusive flow and affinity of the metabolic reaction, according to Carie–Prigogine principle, should be possible if the biological membrane is isotropic. The conclusion, therefore, is that all membranes showing active transport should be anisotropic in nature which actually is the case. Thus anisotropy is one of the chief characteristics of biological membranes.

The first phenomenological treatment of active transport is due to Kedem. The phenomenological equations are written as

$$X_i = \sum_j R_{ij} J_j + R_{ir} J_{ch} \tag{8.198}$$

$$A_f = \sum_i R_{ri} J_j + R_{rr} J_{ch} \tag{8.199}$$

The flows of the solutes and water are represented by J_j and of metabolic reaction by J_{ch}. The metabolically induced transport of a species i is, therefore, dependent upon the rate of chemical reaction and the cross-coefficient R_{ir}. Since A_f the affinity of the reaction and J_{ch} are scalars and X_j and J_j are vectors, R_{ij}, and R_{rr} are scalars. All R_{ir} are, however, vectors and must be zero if the membrane is isotropic. The essential anisotropy of the biological membrane is stressed once again. Let us take up a simple case where the flow of ions 1 and 2 of a 1:1 electrolyte is considered and the flow of water is considered negligible. To simplify matters further it is assumed that there is no coupling between the flow of anion 2 and the chemical reaction or the flow of cation 1 so that $R_{2r} = 0$ and $R_{12} = 0$. Thus, we are limited to consider the active transport of cation. Under these simplifying restrictions the phenomenological equations become

$$\Delta\mu_1 = R_{11} J_1 + R_{1r} J_{ch} \tag{8.200}$$

$$\Delta\mu_2 = R_{22} J_2 \tag{8.201}$$

$$A_f = R_{r1} J_1 + R_{rr} J_{ch} \tag{8.202}$$

In formulating the above equations, the experiments of Ussing and Zerahn were kept in mind. In the frog skin experiments, the bathing solutions were identical chloride Ringer-solutions. Reversible electrodes were inserted in the two compartments, separated by the membrane and short circuited. Under these conditions, a short-circuit current $I = (Z_1 J_1 + Z_2 J_2)F$, where Z_1 and Z_2 are the valencies of the cation 1 and the anion 2, respectively and F is the Faraday, will flow. Since the two bathing solutions are identical $\Delta\mu_1 = \Delta\mu_2 = 0$ and hence from Equation (8.201), $J_2 = 0$. Therefore, the short-circuit current

$$I = Z_1 J_1 F = -\frac{R_{1r}}{R_{11}} J_{ch} F \tag{8.203}$$

Since R_{11}, J_{ch} and F are all positive, I will be positive only when R_{1r} is negative. Thus the force required to drive J_1 is reduced because of coupling in active transport process since R_{1r} J is negative. The short-circuit current is, therefore, equal to the ionic current through the membrane and proportional to the rate of metabolic reaction. These conclusions are consistent with the conclusions

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drawn by Ussing and Zerahn in their experiments on the measurement of net sodium flux under short circuit conditions.

Energetics of active transport

In a simple two flux–two force system, the entropy production σ is written as

$$\sigma = J_1X_1 + J_2X_2 \geq 0 \tag{8.204}$$

If the component 1 is actively transported uphill against its conjugate force X_1 the term J_1X_1 will be negative. The process 2 (which corresponds to the term J_2X_2) is the driving process and the process 1 (which corresponds to the term J_1X_1) is the driven process. Thus the term J_1X_1 is negative or the actively transported component, which therefore, consumes entropy at the expense of the driving process 2. A proportion of the entropy, and so the free energy dissipated by the process 2, is converted into a form characteristic of process 1. The energy so withdrawn may either be stored up within the system in the form of a static head of the force X_1 or it may be dissipated externally by a continuing flow J_1. The efficiency of energy conversion η as defined by Kedem and Caplan may be written as

$$\eta = -\frac{J_1X_1}{J_2X_2} = 1 - \frac{\sigma}{J_2X_2} \tag{8.205}$$

The function η represents the fraction of the entropy production of process 2 utilized by process 1. Since process 1 is driven by process 2, in a direction opposite to its own driving force it is obvious that $0 \leq \eta \leq 1$. The efficiency η is zero both at level flow, when the driving force X_2 = constant and $X_1 = 0$ and at static head when X_2 is held constant and $J_1 = 0$. Between these two limits it has been shown that η passes through a maximum defined by

$$\eta_{max} = \frac{q^2}{\left(1 + \sqrt{1 - q^2}\right)^2} \tag{8.206}$$

where q is called the *degree of coupling* and is defined as

$$q = \frac{L_{12}}{\sqrt{L_{11}L_{22}}} = -\frac{R_{12}}{\sqrt{R_{11}R_{22}}} \tag{8.207}$$

Since the straight coefficients L_{11} and L_{22} are positive and the cross-coefficients L_{12} may be positive or negative, the value of q must lie within the limits $1 \geq q \geq -1$ and should be zero when L_{12} or R_{12} is zero. It follows from Equations (8.206) and (8.207) that as q decreases there is a rapid reduction in η_{max}, which implies that biological systems showing active transport, must have a large degree of coupling. This also leads us to the conclusion that in active processes, cross-coefficients assume importance. The reverse statement, however, is not true, i.e. processes where cross-coefficients are important need not be active processes.

To obtain the value of q it is necessary only to measure the flow J_2 of the

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consequently two flows show that the state of no net flow is the state of minimum entropy production provided the flows are linearly related to forces and Onsager's reciprocal relations are obeyed.

3. Show that in a two-flux two-force systems where linear phenomenological relations are obeyed

$$(L_{12} + L_{21})^2 < 4L_{11}L_{22}$$

where L_{12} are cross-phenomenological coefficients and L_{11} and L_{22} are straight coefficients.

4. Show that all biological membranes showing active transport have to be anisotropic in nature.

5. Discuss the energetics of active transport. What is meant by the degree of coupling? Outline a method for experimental evaluation of degree of coupling.

6. Write down the linear phenomenological equations for electro-osmotic transport in the inverted matrix form and use the theorem of minimum entropy production to deduce the expressions for different steady state effects. Show that Saxen's relation follows on account of Onsager's theorem.

7. What is meant by the term 'reflection coefficient' in an osmometric situation?

   (a) The term refers to the membrane or to the solutions which the membrane separates or to the whole system consisting of membrane separating the solutions.

   (b) What is the minimum and the maximum value which the reflection coefficient can have?

   (c) What is implication if (i) $\sigma = 0$ (ii) $\sigma = 1$ and $\sigma < 1$? Discuss.

   (d) Using an osmometric system consisting of a membrane separating an aqueous solution of a non-electrolyte from the solvent water, a steady hydrostatic pressure equal to 1 atmosphere was observed. If the reflection coefficient (σ) is 0.5 what would be the value of the osmotic pressure of the non-electrolyte solution.

8. Healthy life is steady state and equilibrium means death. Discuss this statement critically.

9. Every growing organism, when it attains maturity (adulthood) it attains a state of minimum entropy production. Discuss this statement critically.

10. What is the principle of detailed balancing in chemical reactions? How does it lead to the principle of microscopic reversibility?

11. In a two-flux two-force system, the two fluxes are J_1 and J_2 and the two conjugate forces are X_1 and X_2. If the same system is represented by an alternative choice of fluxes and forces J'_1, J'_2 and X'_1 and X'_2 such that the new choice is related to the old choice by the following equations:

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$$J_1' = n_1 J_1 + n_2 J_2$$
$$J_2' = n_3 J_1 + n_4 J_2$$
$$X_1' = n_5 X_1 + n_6 X_2$$
$$X_1' = n_7 X_1 + n_8 X_2$$

Show that the following relationship will hold among the constants n_1 to n_8

$$n_1 n_5 + n_3 n_7 = 1$$
$$n_2 n_6 + n_4 n_8 = 1$$
$$n_1 n_6 + n_3 n_8 = 0$$
$$n_2 n_5 + n_4 n_7 = 0$$

Further show that Onsager's relations will also hold for the new choice. Assume linear phenomenological relations.

[*Hint*: Start with the equations $\sigma = J_1 X_1 + J_2 X_2 = J_1' X_1' + J_2' X_2'$.]

12. The phenomenon of electro-osmotic pressure can be viewed as an energy conversion device where the input electrical energy is converted into the output mechanical work.

Show that the efficiency of energy conversion for a fixed value of $\Delta\phi$ across the membrane would be maximum when ΔP developed across the membrane would be half the value of the steady state electro-osmotic pressure. Assume the validity of linear phenomenological relations.

(*Hint*: Write the efficiency of energy conversion η as

$$\eta = -\frac{j_{\text{output}} x_{\text{output}}}{J_{\text{input}} x_{\text{input}}} = -\frac{J_V \Delta P}{I \Delta\phi}$$

$I\Delta\phi$ being fixed η will be zero when either $\Delta P = 0$ or $J_V = 0$, the condition for steady state electro-osmotic pressure. Hence, η if plotted against ΔP should pass through a maximum. To obtain the condition for maximum, put $J_V = L_{11}\Delta P + L_{12}\Delta\phi$ and apply the condition

$$\frac{\partial \eta}{\partial \Delta P} = 0$$

Do a similar exercise for streaming potential and show that

$$(\eta_e)_{\max} = (\eta_s)_{\max}$$

where the subscripts e and s respectively represent electro-osmotic pressure and streaming potential.

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Chapter 9

The Non-linear Region

Two main steps in the methodology of irreversible thermodynamics are: (i) the choice of fluxes and forces from the equation for entropy production obtained from Gibbs equation and (ii) to write the phenomenological relationship between fluxes and forces. Gibbs equation was actually deduced for the systems in equilibrium and its use for the non-equilibrium situations is definitely a new postulate. The linear phenomenological laws are also valid only in the neighbourhood of equilibrium and as a matter of fact, in most cases, represent only an approximate functional relationship between fluxes and forces. In many cases the linear relationships between fluxes and forces do not conform to the physical reality, e.g. the linear relationship between chemical reaction rate and affinity is only a particular case of the generalized exponential relationship and is valid only when the reaction is close to equilibrium. Therefore, the non-equilibrium thermodynamic treatment based on linear laws and Gibbs equation has only a limited domain of validity. One way of extending the domain of validity of what may be called linear thermodynamics of irreversible processes is to consider generalized non-linear relationships between fluxes and forces. But this is feasible only if Gibbs equation has a larger domain of validity than that of linear laws, because even for writing non-linear rate equations, conjugate fluxes and forces will have to be picked up from the equation for entropy production obtained from Gibbs equation. Fortunately, Gibbs equation has a larger domain of validity than that of linear laws. This fact has been well brought out in literature.

9.1 NON-LINEAR FLUX EQUATIONS

Thus it is possible to extend the domain of non-equilibrium thermodynamics, of course, within the domain of validity of Gibbs equation, by considering the non-linear phenomenological equations instead of linear ones. The major question that crops up is that what should be the generalized form of non-linear phenomenological equations. Li invoked the concept of macroscopic separability and showed using Taylors expansion of flows around equilibrium; if any flow J_i is a function of the forces $X_1, X_2, \ldots$, then

$$J_i = \sum_j^{\prime} L_{ij} X_j + \frac{1}{2} \sum_j \sum_k L_{ijk} X_j X_k + \cdots, \tag{9.1}$$

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where L_{ij} and L_{ijk} are the derivatives of various orders of J given by

$$L_{ij} = \left(\frac{\partial J_i}{\partial X_j}\right)_0 ; \qquad L_{ijk} = \left(\frac{\partial^2 J_i}{\partial X_j \partial X_k}\right)_0 \tag{9.2}$$

The subscript 0 denotes the values of the derivatives at equilibrium. Li has shown that Onsager's reciprocal relations, second-order symmetry and third-order symmetry, etc., viz.,

$$L_{ij} = L_{ji}; \quad L_{ijk} = L_{jik} = L_{jki} \tag{9.3}$$

$$L_{ijkl} = L_{ijlk} = L_{ikjl} = L_{jikl} \tag{9.4}$$

follow as a mathematical consequence under certain condition. Any total process can always be viewed as some combination of the independent processes going on in the system. Li's analysis shows that the independent process involved have the νth-order independence if the νth order coefficients are symmetric.[1]

The following simple examples, may help to clarify the analysis. Let us take a simple case where two fluxes and two conjugate forces are operative. Let J_1 and J_2 be the fluxes and X_1 and X_2 the corresponding forces of the two independent processes going on in the system. The rate equation for the independent processes can then be deduced using Taylor's expansion of flows around equilibrium. Since J_1 is a function of X_1 only and J_2 is a function of X_2 only, we can write

$$J_1 = \left(\frac{\partial J_1}{\partial X_1}\right)_0 X_1 + \frac{1}{2!}\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0 X_1^2 + \cdots. \tag{9.5}$$

$$J_2 = \left(\frac{\partial J_2}{\partial X_2}\right)_0 X_2 + \frac{1}{2!}\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0 X_2^2 + \cdots. \tag{9.6}$$

where the subscript 0 refers to the values at the equilibrium state. Let the fluxes J_1' and J_2' and the forces X_1' and X_2' of the total process be the linear combination of the fluxes J_1 and J_2 and the forces X_1 and X_2 of the independent processes represented by the equations

$$\left.\begin{aligned} J_1' &= n_1 J_1 + n_2 J_2 \\ J_2' &= n_3 J_1 + n_4 J_2 \\ X_1' &= n_5 X_1 + n_6 X_2 \\ X_2' &= n_7 X_1 + n_8 X_2 \end{aligned}\right\} \tag{9.7}$$

where n_s are integers. Since the value of entropy production σ should remain unaltered, we get

$$\sigma = J_1 X_1 + J_2 X_2 = J_1' X_1' + J_2' X_2' \tag{9.8}$$

1. Li, J.C.M., *J. Chem. Phys.*, 29 (1958) 747, *J. Appl. Phys.* 33 (1962) 616.

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Therefore, we have

$$\left.\begin{aligned} n_1n_5 + n_3n_7 &= 1 \\ n_2n_6 + n_4n_8 &= 1 \\ n_1n_6 + n_3n_8 &= 0 \\ n_2n_5 + n_4n_7 &= 0 \end{aligned}\right\} \tag{9.9}$$

From Equations (9.5)–(9.7), we can write

$$J_1' = L_{11}X_1' + L_{12}X_2' + L_{111}X_1'^2 + L_{122}X_2'^2 + L_{112}X_1'X_2' + \cdots. \tag{9.10}$$

$$J_2' = L_{21}X_1' + L_{22}X_2' + L_{211}X_1'^2 + L_{222}X_2'^2 + L_{212}X_1'X_2' + \cdots. \tag{9.11}$$

where

$$L_{11} = \frac{1}{n_5n_8 - n_6n_7}\left[n_1n_8\left(\frac{\partial J_1}{\partial X_1}\right)_0 - n_2n_7\left(\frac{\partial J_2}{\partial X_2}\right)_0\right]$$

$$L_{12} = \frac{1}{n_5n_8 - n_6n_7}\left[n_2n_5\left(\frac{\partial J_2}{\partial X_2}\right)_0 - n_1n_6\left(\frac{\partial J_1}{\partial X_1}\right)_0\right]$$

$$L_{111} = \frac{1}{(n_5n_8 - n_6n_7)^2}\left[\frac{n_1n_8^2}{2!}\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0 + \frac{n_2n_7^2}{2!}\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right]$$

$$L_{112} = \frac{1}{(n_5n_8 - n_6n_7)^2}\left[-n_2n_5n_7\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0 - n_1n_6n_8\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0\right]$$

$$L_{21} = \frac{1}{n_5n_8 - n_6n_7}\left[-n_4n_7\left(\frac{\partial J_2}{\partial X_2}\right)_0 + n_3n_8\left(\frac{\partial J_1}{\partial X_1}\right)_0\right]$$

$$L_{211} = \frac{1}{(n_5n_8 - n_6n_7)^2}\left[\frac{n_3n_8^2}{2!}\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0 + \frac{n_4n_7^2}{2!}\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right]$$

$$L_{222} = \frac{1}{(n_5n_8 - n_6n_7)^2}\left[\frac{n_3n_6^2}{2!}\left(\frac{\partial^2 J_1}{\partial X_1}\right)_0 + \frac{n_4n_5^2}{2!}\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right]$$

$$L_{212} = \frac{1}{(n_5n_8 - n_6n_7)^2}\left[-n_3n_6n_8\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0 - n_4n_5n_7\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right]$$

$$L_{122} = \frac{1}{(n_5n_8 - n_6n_7)^2}\left[\frac{n_1n_6^2}{2!}\left(\frac{\partial^2 J_1}{\partial X_1^2}\right)_0 + \frac{n_2n_5^2}{2!}\left(\frac{\partial^2 J_2}{\partial X_2^2}\right)_0\right]$$

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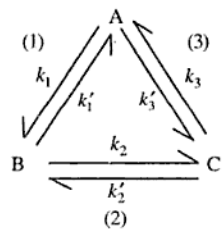
$$L_{22} = \frac{1}{n_5 n_8 - n_6 n_7}\left[n_4 n_5 \left(\frac{\partial J_2}{\partial X_2}\right)_0 - n_3 n_6 \left(\frac{\partial J_1}{\partial X_1}\right)_0 \right]$$

From Equation (9.9), it can be seen that

$$L_{12} = L_{21}; \quad L_{112} = 2L_{211}; \quad L_{212} = 2L_{122} \tag{9.12}$$

Since we have considered up to second-order independence in the independent processes, Onsager's relations and second-order symmetries automatically follow. By taking the examples of chemical reactions and following the methods of chemical kinetics, it has been possible to demonstrate[2] that if independent processes have nth order independence the coefficients up to nth order are completely symmetric. Two cases of chemical reactions: one in which the independent processes had only first-order independence and the other in which the independent processes had up to nth order independence were considered and it was shown that in the former case, only Onsager's symmetries were obeyed whereas in the latter case Onsager's symmetries and also higher-order symmetries were obeyed.

Consider a monomolecular triangular reaction of the type:



where k_1, k_2, k_3 are the specific reaction rates for the forward reactions while k_1', k_2', k_3' are those for the reverse reactions. Let x_A, x_B, x_C be the mole fractions of the species A, B and C at any instant. Further let A_1, A_2 and A_3 be the affinities of the reactions (1), (2) and (3), respectively. These are related to the chemical potentials μ of the various species denoted by the subscripts

$$A_1 = \mu_A - \mu_B; \quad A_2 = \mu_B - \mu_C; \quad A_3 = \mu_C - \mu_A \tag{9.13}$$

From Equation (9.13) it follows that

$$A_3 = -(A_1 + A_2) \tag{9.14}$$

Denoting the equilibrium quantities by the subscript 0 we can write

2. Rastogi, R.P., Srivastava, R.C. and Singh, K., *Trans. Faraday Soc.*, 61 (1965) 854.

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$$\left.\begin{aligned} x_A &= x_A^0 \exp\ \frac{\mu_A - \mu_A^0}{RT} \\ x_B &= x_B^0 \exp\ \frac{\mu_B - \mu_B^0}{RT} \\ x_C &= x_C^0 \exp\ \frac{\mu_C - \mu_C^0}{RT} \end{aligned}\right\} \tag{9.15}$$

From Equation (9.15), it follows that

$$x_A : x_B : x_C = x_A^0 \exp\ \frac{A_1}{RT} : x_B^0 : x_C^0 \exp\left(-\frac{A_2}{RT}\right) \tag{9.16}$$

But since

$$x_A + x_B + x_C = 1 \tag{9.17}$$

we get on solving Equation (9.16)

$$x_A = \frac{x_A^0 \exp\,(A_1/RT)}{x_A^0 \exp\,(A_1/RT) + x_C^0 \exp\,(-A_2/RT) + x_B^0} \tag{9.18}$$

$$x_B = \frac{x_B^0}{x_A^0 \exp\,(A_1/RT) + x_C^0 \exp\,(-A_2/RT) + x_B^0} \tag{9.19}$$

$$x_C = \frac{x_C^0 \exp\,(-A_2/RT)}{x_A^0 \exp\,(A_1/RT) + x_C^0 \exp\,(-A_2/RT) + x_B^0} \tag{9.20}$$

The chemical reaction rates J_1, J_2 and J_3 for the reactions (1), (2) and (3) are, therefore,

$$J_1 = k_1 x_A - k_1' x_B = k_1 x_A^0 \frac{A_1}{RT}\left[1 + \frac{1-2x_A^0}{2}\frac{A_1}{RT} + x_C^0 \frac{A_2}{RT} + \frac{1-6x_A^0}{6}\left(\frac{A_1}{RT}\right)^2 - \frac{1}{2}x_C^0\left(\frac{A_2}{RT}\right)^2 + \frac{1}{2}x_C^0 \frac{A_1}{RT}\frac{A_2}{RT} + \ldots.\right] \tag{9.21}$$

$$J_2 = k_2 x_B - k_2' x_C = k_2 x_B^0 \frac{A_2}{RT}\left[1 - x_A^0 \frac{A_1}{RT} + \frac{2x_C^0 - 1}{2}\frac{A_2}{RT} - \frac{1}{2}x_A^0\left(\frac{A_1}{RT}\right)^2 + \frac{1-6x_C^0}{6}\left(\frac{A_2}{RT}\right)^2 + \frac{1}{2}x_A^0 \frac{A_1}{RT}\frac{A_2}{RT} + \ldots.\right] \tag{9.22}$$

$$J_3 = k_3 x_C - k_3' x_A = k_3 x_C^0 \frac{A_3}{RT}\left[1 - \frac{2x_A^0 - 1}{2}\frac{A_1}{RT} + \frac{2x_C^0 - 1}{2}\frac{A_2}{RT} + \frac{1-6x_A^0}{6}\left(\frac{A_1}{RT}\right)^2\right.$$

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$$+\frac{1-6x_C^0}{6}\left(\frac{A_2}{RT}\right)^2+\frac{3\left(x_A^0+x_C^0\right)-1}{6}\frac{A_1}{RT}\frac{A_2}{RT}+\cdots\Bigg] \quad (9.23)$$

Using the relations at equilibrium:

$$k_1x_A^0=k_1'x_B^0; \qquad k_2x_B^0=k_2'x_C^0; \qquad k_3x_C^0=k_3'x_A^0$$

the relations (9.21)–(9.23) show that chemical reaction rates can be expressed as power series in affinity which is identical with Li's Taylor type expansion.

In triangular isomerization reactions one can only measure the instantaneous concentration of A, B and C. The rate of change of these species is related to J_1, J_2 and J_3. Thus

$$J_1-J_3=-\frac{dx_A}{dt}; \qquad J_2-J_3=\frac{dx_C}{dt} \quad (9.24)$$

The quantities (J_1-J_3) and (J_2-J_3) are new flows. The corresponding forces can be found as follows: the entropy production σ can be written as

$$T\sigma = J_1A_1+J_2A_2+J_3A_3 \quad (9.25)$$

which, using Equation (9.14), can be transformed into

$$T\sigma = \left(J_1-J_3\right)A_1+\left(J_2-J_3\right)A_2 \quad (9.26)$$

Hence the new forces are A_1 and A_2. From Equations (9.21)–(9.23), we can write

$$\begin{aligned}J_1-J_3=&\left(k_1x_A^0+k_3x_C^0\right)\frac{A_1}{RT}+k_3x_C^0\frac{A_2}{RT}+\left[\frac{1-2x_A^0}{2}\left(k_1x_A^0+k_3x_C^0\right)\right]\left(\frac{A_1}{RT}\right)^2\\&+\left(k_3x_C^0\frac{2x_C^0-1}{2}\right)\left(\frac{A_2}{RT}\right)^2+\left[k_1x_A^0x_c^0+k_3x_C^0\left(x_C^0-x_A^0\right)\right]\frac{A_1}{RT}\frac{A_2}{RT}\\&+\left[\frac{1-6x_A^0}{6}\left(k_1x_A^0+k_3x_C^0\right)\right]\left(\frac{A_1}{RT}\right)^3+k_3x_C^0\frac{1-6x_C^0}{6}\left(\frac{A_2}{RT}\right)^3\\&-\frac{1}{2}\left[k_1x_A^0x_C^0+k_3x_C^0\left(x_C^0-x_A^0\right)\right]\frac{A_1}{RT}\left(\frac{A_2}{RT}\right)^2\\&+\frac{1}{2}\left[k_1x_A^0x_C^0+k_3x_C^0\left(x_C^0-x_A^0\right)\right]\left(\frac{A_1}{RT}\right)^2\frac{A_2}{RT}+\cdots\end{aligned} \quad (9.27)$$

$$\begin{aligned}J_2-J_3=&k_3x_C^0\frac{A_1}{RT}+\left(k_2x_B^0+k_3x_C^0\right)\frac{A_2}{RT}-k_3x_C^0\frac{2x_A^0-1}{2}\left(\frac{A_1}{RT}\right)^2\\&+\left[\frac{2x_C^0-1}{2}\left(k_2x_B^0+k_3x_C^0\right)\right]\left(\frac{A_2}{RT}\right)^2+\left[k_3x_C^0\left(x_C^0-x_A^0\right)-k_2x_B^0x_A^0\right]\frac{A_1}{RT}\frac{A_2}{RT}\end{aligned}$$

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$$J_1' = L_{11}\frac{A_1'}{RT} + L_{12}\frac{A_{II}'}{RT} + L_{111}\left(\frac{A_1'}{RT}\right)^2 + L_{122}\left(\frac{A_{II}'}{RT}\right)^2 + L_{112}\frac{A_1'}{RT}\frac{A_{II}'}{RT} + L_{1111}\left(\frac{A_1'}{RT}\right)^3 + L_{1222}\left(\frac{A_{II}'}{RT}\right)^3 + L_{1112}\left(\frac{A_1'}{RT}\right)^2\frac{A_{II}'}{RT} + L_{1122}\frac{A_1'}{RT}\left(\frac{A_{II}'}{RT}\right)^2 + \cdots \quad (9.35)$$

and

$$J_{II}' = L_{21}\frac{A_1'}{RT} + L_{22}\frac{A_{II}'}{RT} + L_{211}\left(\frac{A_1'}{RT}\right)^2 + L_{222}\left(\frac{A_{II}'}{RT}\right)^2 + L_{212}\frac{A_1'}{RT}\frac{A_{II}'}{RT} + L_{2111}\left(\frac{A_1'}{RT}\right)^3 + L_{2222}\left(\frac{A_{II}'}{RT}\right)^3 + L_{2112}\left(\frac{A_1'}{RT}\right)^2\frac{A_{II}'}{RT} + L_{2122}\frac{A_1'}{RT}\left(\frac{A_{II}'}{RT}\right)^2 + \cdots. \quad (9.36)$$

where

$$L_{11} = \frac{1}{4}\left(k_1 x_A^0 + k_2 x_C^0\right)$$

$$L_{12} = \frac{1}{4}\left(k_1 x_A^0 - k_2 x_C^0\right)$$

$$L_{111} = \frac{1}{16}\left[k_1 x_A^0\left(1-2x_A^0\right) + k_2 x_C^0\left(1-2x_C^0\right)\right]$$

$$L_{122} = \frac{1}{16}\left[k_1 x_A^0\left(1-2x_A^0\right) + k_2 x_C^0\left(1-2x_C^0\right)\right]$$

$$L_{112} = \frac{1}{8}\left[k_1 x_A^0\left(1-2x_A^0\right) - k_2 x_C^0\left(1-2x_C^0\right)\right]$$

$$L_{1111} = \frac{1}{96}\left[k_1 x_A^0\left(1-6x_A^0\right) + k_2 x_C^0\ \left(1-6x_C^0\right)\right]$$

$$L_{1222} = \frac{1}{96}\left[k_1 x_A^0\left(1-6x_A^0\right) - k_2 x_C^0\left(1-6x_C^0\right)\right]$$

$$L_{1112} = \frac{1}{32}\left[k_1 x_A^0\left(1-6x_A^0\right) - k_2 x_C^0\left(1-6x_C^0\right)\right]$$

$$L_{1122} = \frac{1}{32}\left[k_1 x_A^0\left(1-6x_A^0\right) + k_2 x_C^0\left(1-6x_C^0\right)\right]$$

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and

$$L_{21} = \frac{1}{4}\left(k_1 x_A^0 - k_2 x_C^0\right)$$

$$L_{22} = \frac{1}{4}\left(k_1 x_A^0 + k_2 x_C^0\right)$$

$$L_{211} = \frac{1}{16}\left[k_1 x_A^0\left(1-2x_A^0\right) - k_2 x_C^0\left(1-2x_C^0\right)\right]$$

$$L_{222} = \frac{1}{16}\left[k_1 x_A^0\left(1-2x_A^0\right) - k_2 x_C^0\left(1-2x_C^0\right)\right]$$

$$L_{212} = \frac{1}{8}\left[k_1 x_A^0\left(1-2x_A^0\right) + k_2 x_C^0\left(1-2x_C^0\right)\right]$$

$$L_{2111} = \frac{1}{96}\left[k_1 x_A^0\left(1-6x_A^0\right) - k_2 x_C^0\left(1-6x_C^0\right)\right]$$

$$L_{2222} = \frac{1}{96}\left[k_1 x_A^0\left(1-6x_A^0\right) + k_2 x_C^0\left(1-6x_C^0\right)\right]$$

$$L_{2112} = \frac{1}{32}\left[k_1 x_A^0\left(1-6x_A^0\right) + k_2 x_C^0\left(1-6x_C^0\right)\right]$$

$$L_{2122} = \frac{1}{32}\left[k_1 x_A^0\left(1-6x_A^0\right) - k_2 x_C^0\left(1-6x_C^0\right)\right]$$

It can be seen that in addition to Onsager's relations second- and third-order symmetries are also satisfied, i.e.

$$L_{12} = L_{21}; \qquad L_{112} = 2L_{211}; \qquad L_{212} = 2L_{122} \tag{9.37}$$

$$3L_{1222} = L_{2122}; \qquad L_{1122} = L_{2112}; \qquad 3L_{2111} = L_{1112} \tag{9.38}$$

Li has outlined a method of identifying independent process using the principle of macroscopic separability. For example, in a two flux–two force system, if we consider only up to second-order terms, i.e.

$$J_1 = L_{11}X_1 + L_{12}X_2 + \frac{1}{2}L_{111}X_1^2 + \frac{1}{2}L_{122}X_2^2 + L_{112}X_1X_2 \tag{9.39}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + \frac{1}{2}L_{211}X_1^2 + \frac{1}{2}L_{222}X_2^2 + L_{212}X_1X_2 \tag{9.40}$$

the relationships

$$L_{12} = L_{21}; \qquad L_{112} = L_{211}; \qquad L_{122} = L_{212} \tag{9.41}$$

and

$$\begin{vmatrix} L_{11} & L_{12} & L_{22} \\ L_{111} & L_{112} & L_{122} \\ L_{211} & L_{212} & L_{222} \end{vmatrix} = 0 \tag{9.42}$$

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$$\left(\frac{\partial \psi}{\partial X_1}\right)_{X_2} = L_{11}X_1 + L_{12}X_2 + \frac{1}{2}L_{111}X_1^2 + \frac{1}{2}L_{122}X_2^2 + L_{112}X_1X_2 = J_1 \quad (9.51)$$

From Equation (9.51) it follows that $\left(\frac{\partial \psi}{\partial X_1}\right)_{X_2}$ being zero is equivalent to $J_1 = 0$. This provides a criterion for evaluating the steady state and should serve as counterpart of the theorem of minimum entropy production in the non-linear region for evaluating steady state. Since ψ is positive definite in accordance with the second law, $\left(\frac{\partial \psi}{\partial X_1}\right)_{X_2}$ b eing equal to zero would represent the condition of a minimum. In general, where we consider the generalized non-linear phenomenological Equation (9.1), the Equation (9.51) would read as

$$\left(\frac{\partial \psi}{\partial X_j}\right)_{X'} = J_j \quad (9.52)$$

where the subscript X' stands for all forces except X_j. It should be admitted that integrability of Equation (9.50) is a consequence of first- and higher-order symmetry relations between the phenomenological coefficients. However, if the integrability of Equation (9.50) can be ascertained by some other physical hypothesis, such as the one similar to that of Caratheodery, then the total symmetry of phenomenological coefficients will be the result of such a hypothesis. It has been accomplished by Li. Therefore, evaluating all the derivatives of ψ in the equilibrium state, we can write

$$\left(\frac{\partial \psi}{\partial X_i}\right)_{X'} = J_j = 0 \quad (9.53)$$

$$\left(\frac{\partial^2 \psi}{\partial X_i \partial X_j}\right)_{X'} = \left(\frac{\partial J_i}{\partial X_j}\right)_{X'} = L_{ij} \quad (9.54)$$

$$\left(\frac{\partial^3 \psi}{\partial X_i \partial X_j \partial X_k}\right)_{X'} = \left(\frac{\partial^2 J_i}{\partial X_j \partial X_k}\right)_{X'} = L_{ijk} \quad (9.55)$$

Equations (9.54) and (9.55) give, respectively, the first- and second-order symmetry relations. Since ψ is a function of state, it can be proved that $d\psi/dt$ can only be negative or zero without using the steady-state condition that the J_j, that corresponds to the unprescribed forces X_j, are all zero. This property is the same as the one possessed by the entropy production σ in the linear region.

It can be demonstrated that when the phenomenological equations are linear and the values of the coefficients are constant, the thermo-kinetic potential ψ reduces to exactly one half of σ. In case of two flux–two force system the thermo-kinetic potential ψ in the linear region is given by

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Similar information can be obtained from the measurements of the streaming potential and current:

$$\left(\frac{\Delta\varphi}{\Delta P}\right)_{I=0} = -\frac{L_{21}}{L_{22}} - \frac{L_{211}}{2L_{22}}\frac{\Delta P}{T} - \frac{L_{212}}{L_{22}}\frac{\Delta\varphi}{T} - \frac{L_{222}}{2L_{22}}\frac{(\Delta\varphi)^2}{T\Delta P} + \cdots \quad (9.65)$$

and

$$\left(\frac{I}{\Delta P}\right)_{\Delta\varphi=0} = \frac{L_{21}}{T} + \frac{1}{2}\frac{L_{211}}{T^2}\frac{\Delta P}{T} + \cdots. \quad (9.66)$$

When the second-order terms are negligible, Equations (9.65) and (9.66) reduce to

$$\left(\frac{\Delta\varphi}{\Delta P}\right)_{I=0} = -\frac{L_{21}}{L_{22}} \quad (9.67)$$

$$\left(\frac{I}{\Delta P}\right)_{\Delta\varphi=0} = \frac{L_{21}}{T} \quad (9.68)$$

The mathematical stratagem, as given by Equations (9.61)–(9.68) was utilized to evaluate the first- and second-order phenomenological coefficients in an acetone/pyrex sinter G4 membrane system. The second-order coefficient L_{112} was evaluated using Equations (9.63) and (9.64). It was found that the range of validity of Poiseuille's law was so large that the coefficient L_{111} was zero. It was also discovered that up to $\Delta\varphi = 440$ volts the coefficient (L_{122}/T^2) was zero. Imposing these conditions and using Equations (9.63) and (9.64), (L_{112}/T^2) was evaluated. The streaming potential measurements showed that up to $\Delta P = 100$ cm of acetone no non-linearity arose. The values of L_{12} and L_{21} were found to be equal confirming Onsager's relations. The non-linear phenomenological relations were also tested by comparing the experimentally determined values of $(J_v)_{\text{total}}$ with those computed using Equation (9.63) and the experimentally determined values of $(J_v)_{\Delta P=0}$ and $(J_v)_{\Delta\varphi=0}$. Experiments on the electro-osmosis of acetone through a pyrex sinter G4 membrane were further refined and the precision of the expansion given by Equation (9.1) was tested. Data on electro-osmotic flow, $(J_v)_{\Delta P=0}$, were shown to be represented by Equation (9.62). The total flow (J_v) was, however, represented by the equation

$$J_v = L_{11}\frac{\Delta P}{T} + L_{12}\frac{\Delta\varphi}{T} + L_{112}\frac{\Delta P}{T}\frac{\Delta\varphi}{T} + \frac{1}{2}L_{122}\left(\frac{\Delta\varphi}{T}\right)^2 + \frac{1}{2}L_{1112}\left(\frac{\Delta P}{T}\right)^2\frac{\Delta\varphi}{T} + \frac{1}{2}L_{1122}\frac{\Delta P}{T}\left(\frac{\Delta\varphi}{T}\right)^2 \quad (9.69)$$

The various phenomenological coefficients occurring in these equations were also evaluated. From streaming potential data for which the linear terms

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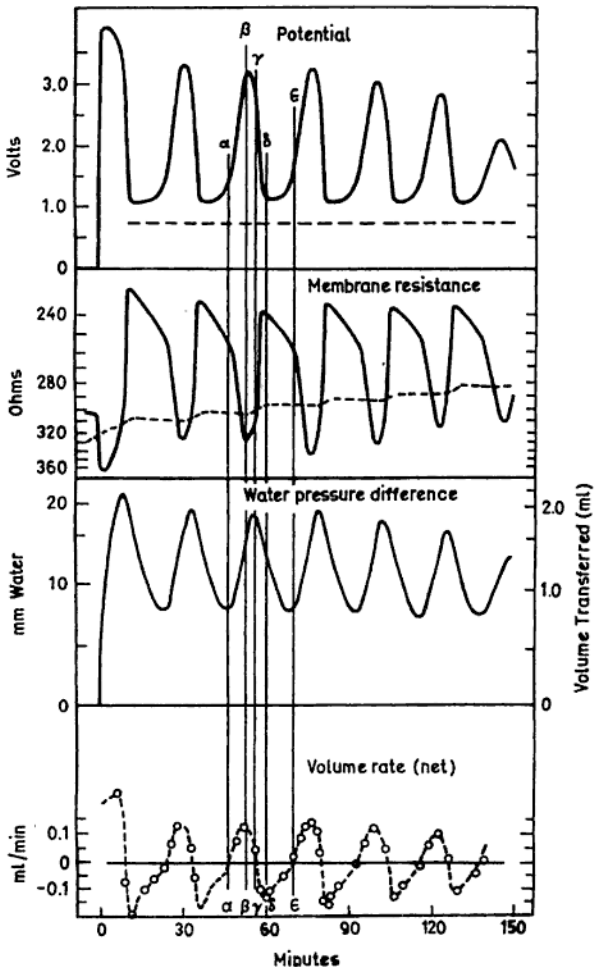

Figure 9.1 Undamped oscillations obtained with the membrane oscillator. Open circles on the volume rate curve calculated from Teorell's equations. Vertical lines illustrate phase relationships. The dashed line in the potential figure represents a correction of the zero voltage level necessitated by the presence of solution between the electrodes and the membrane. The dashed line in the membrane resistance figure represents the resistance in compartment II [refer to Teorell, T., *J. Gen. Physiol*, 42 (1959) 831, 847].

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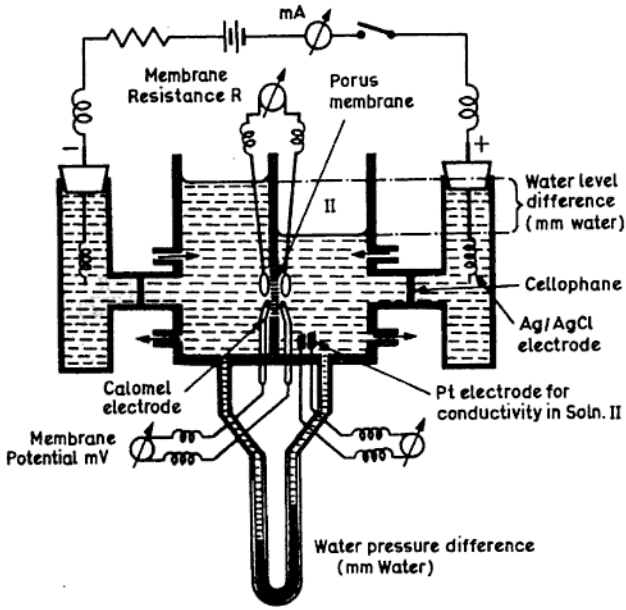

Figure 9.2 The experimental arrangement for the membrane oscillator. [Teorell, T., *J. Gen. Physiol*, 42 (1959) 831].

9.4.2 The Origin of Oscillations[10]

Let us consider the second-order equation

$$M\ddot{x} + R\dot{x} + Cx = 0 \tag{9.70}$$

for the motion of a linear spring after displacement from its equilibrium position. In Equation (9.70), first term on left-hand side is the inertial force, second the resistive or frictional force and third is the restoring or spring force. Equation (9.70) states that the sum of all forces acting on the spring equals zero. In Equation (9.70), M is the mass of the spring, R is the resistance or the friction coefficient and C is the spring constant. Equation (9.70) can be generated by the following two first-order differential equations:

$$\frac{dx}{dt} = ax + by \tag{9.71}$$

$$\frac{dy}{dt} = cx + dy \tag{9.72}$$

10. This analysis is by Caplan, S.R. and Mikulecky, D.C., in *Ion Exchange* Vol. I, edited by J.A. Marinsky, Marcel-Dekker, New York (1966) pp. 1-64.

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The desired second-order differential equation in x can be obtained by differentiating Equation (9.71) with respect to time and making appropriate substitution from Equation (9.72) to eliminate y. When this is done it turns out that

$$M \equiv 1 \tag{9.73}$$

$$R \equiv -(a + d) \tag{9.74}$$

$$C \equiv ad - bc \tag{9.75}$$

The general solution to Equation (9.70) is

$$x = \exp\left(\frac{-Rt}{2M}\right)\left(A_1 \exp\left\{t\left[\left(\frac{R}{2M}\right)^2 - \frac{C}{M}\right]^{1/2}\right\}\right) + A_2 \exp\left\{-t\left[\left(\frac{R}{2M}\right)^2 - \frac{C}{M}\right]^{1/2}\right\} \tag{9.76}$$

where A_1 and A_2 are arbitrary constants to be determined by the initial values of x and dx/dt. The periodic solution arises when the expression under the radical in Equation (9.76) is negative, i.e.

$$\frac{C}{M} > \left(\frac{R}{2M}\right)^2 \tag{9.77}$$

In view of relations (9.73) to (9.75), we can write from Equation (9.77)

$$bc < 0 \tag{9.78}$$

and

$$|bc| > \frac{(a-d)^2}{4} \tag{9.79}$$

Thus the oscillations arise from a particular coupling between the processes such that when one is in its equilibrium position, the other tends to drag it out. If the coupling allows the energy transfer to be complete the oscillations are sustained or undamped ($a = -d$). In the context of Equation (9.70), it corresponds to $R = 0$, i.e. there is no friction. If $R > 0$, the oscillation will damp out in time unless another process is present and coupled in such a way that it continually supplies energy to the system.

If we consider an osmometric set-up and identify x and y with ΔP and $\Delta\Pi$; P and Π being the pressure and the osmotic pressure respectively, the volume flow J_V can be identified with $\frac{d(\Delta P)}{dt}$ multiplied by some factor determined by the geometry of the system. A similar argument can be applied to show the flow of solute can be identified with $\frac{d(\Delta\Pi)}{dt}$ multiplied by some positive factor. In this way, a, b, c and d in Equations (9.71) and (9.72) can be identified with L_{11}, L_{12}, L_{21} and L_{22} (see Chapter 8) divided by the appropriate capacity factors respectively. From this identification, it is readily seen that the phenomenological coefficients can never fulfil the requirements of a linear periodic system if they are symmetrical. This is due to the fact that periodicity is possible only when b and c (or L_{12} and L_{21}) have opposite signs.

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Chapter 10

Network Thermodynamics

Network thermodynamics, in which classical and irreversible thermodynamics are combined with the modern network theory, is one of the last great contributions of Prof. A.K. Katchalsky. This, no doubt, was based on the pioneering ideas of Meixner who was the first to notice the connection between irreversible transport systems and electrical networks. This is relatively a recent development and to the best of our knowledge the brief monograph by Schnakenberg is the only text on the subject so far.

Network analogs for continuous systems have been a long-standing tool in engineering, physiology, physics and in many other disciplines. The success of these analogs in emulating the dynamical behaviour was not accidental. This was a natural consequence of the underlying unity in the mathematical description of all dynamical theories. The linear graph notation, which is the conventional technique in the network theory, is not always suited for the irreversible thermodynamic systems. For such situations, an alternative procedure of bond graphs which takes into consideration the transduction of energy from one form to another is employed instead. The generation and elucidation of bond graph representations are much more than mere pictorial representations of physical systems. These diagrams highlight systems topology and are actually another notation for the dynamical equations themselves.

The purpose of this chapter is to summarize the elements of network thermodynamics and to demonstrate, by choosing a few typical examples, its application to transport process, particularly the coupled transport processes.

10.1 THE FORMALISM

The energy of a thermodynamic system is altered by interaction with its surroundings. The interaction is via two modes—the energy transfer as work, and the energy transfer as heat. Each such interaction mode is referred to as an energy port and each such port is characterized by a pair of variables. For example, the mechanical energy port will have p and v (pressure and volume) as variables and the thermal energy port will have T and S (temperature and entropy) as variables. The fact that variables come in pairs is in keeping with the circuit theory where one port is called a *two-terminal device*. Since more than one work modes are possible, a thermodynamic system can be visualized as a multi-port system.

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In the network approach, if a system is continuous, it is conceptually separated into reversible and irreversible subsystems. The reversible subsystems store energy without loss and the irreversible ones dissipate energy without storage, each of these subsystems is identified with n-port. To facilitate graphical notation for interconnecting n-ports, each port is represented by an ideal energy bond. For example, a thermo-mechanical two-port is graphically represented as shown in Figure 10.1. The ideal energy bonds (Figure 10.1) are a generalization of perfectly conducting wires or infinitely stiff rods or such ideal connectors which transmit power instantaneously from one element to another without any loss or storage in between any two elements.

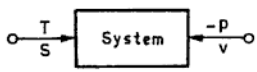

Figure 10.1 A thermo-mechanical two-port system.

10.1.1 The State Variables

Here we consider the problem of defining the dynamical variables for the description of the system. Equilibrium thermodynamics defines a unique state function, the internal energy, U, as a function of several thermodynamic displacement q_i, viz., the entropy S, the volume V, the number of moles (N_i) of the various components constituting the systems. That is

$$U(S, V, N_1, N_2, ..., N) \equiv U(q_1, q_2, ..., q_n) \tag{10.1}$$

The displacements of classical thermodynamics and the differentials of U with respect to displacements which define conjugate potentials are taken as new state variables in network thermodynamics. The Gibb's equation easily follows from Equation (10.1) in the light of these definitions, i.e.

$$dU = \sum_{i=1}^{n} \frac{\partial U}{\partial q_i} d_{q_i} \equiv T\,dS - p\,dV + \sum \mu_i dN_i \tag{10.2}$$

There is a striking point of difference with the procedure followed in non-equilibrium thermodynamics. In non-equilibrium thermodynamics, a dynamical theory is obtained from an equilibrium relation—the conjugate fluxes and forces are chosen by transforming the time derivative of Gibb's equation. In network thermodynamics, one goes the other way, i.e. one starts with a dynamical theory from which the equilibrium theory can be deduced—the deduction of Equation (10.2). This certainly is a more straightforward approach.

The fundamental thermodynamic quantity in network approach is energy rate instead of energy. The energy rate or power P transmitted, stored or dissipated, is finite and can be expressed as a product of an effort or a force variable 'e' and a flow variable 'f'. Thus,

$$P = ef \tag{10.3}$$

The terms e and f are in fact borrowed from circuit theory and are also called 'across' and 'through' variables respectively. In an electrical network, the variables

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e and f are respectively the voltage difference and the current, in diffusional processes chemical potential difference ($\Delta\mu_i$) and the mass flow, in chemical reactions; affinity and the reaction rate and so on. The variables e and f can be related to the generalized momentum P and the generalized displacement q by the equations

$$p(t) \equiv p(0) + \int_0^t e(t)\, dt \tag{10.4}$$

and

$$q(t) \equiv q(0) + \int_0^t f(t)\, dt \tag{10.5}$$

For example, in the case of chemical reactions, ζ is the generalized displacement variable and can be related to the flow variable, the chemical reaction rate J_r by the equation

$$\zeta(t) = \zeta(0) + \int_0^t J_r\, dt \tag{10.6}$$

Since the e and f variables are the counterparts of voltage difference and current in electrical network, these must also obey the Kirchhoff voltage law (KVL) and the Kirchhoff current law (KCL).

10.1.2 Constitutive Relations

In order that the state variables may be utilized to describe the behaviour of actual systems, one must know the functional relations between them. These relationships are called *constitutive relations* or *equations of state*. Constitutive relationships, in fact, are relationships between a KCL variable (f or q) and a KVL variable (e or p). These are obtained either experimentally or theoretically. Let us consider two kinds of energetic transactions of interest in thermodynamics

$$E_c(t) = \int_0^t ef\, dt = \int_{q(0)}^{q(t)} e\, dq \tag{10.7}$$

and

$$E_R(t) = \int_0^t ef\, dt \tag{10.8}$$

Equation (10.7) gives the capacitative energy storage and Equation (10.8) gives the energy dissipation. To integrate Equation (10.7), one requires capacitative constitutive relations between displacement and the charge variable of the form

$$q = \psi_c(e) \tag{10.9}$$

Any element which stores energy by virtue of a generalized displacement is called a *capacitor* and denoted by C, e.g. a volume element which attains a chemical potential by virtue of mass flow as in a membrane. From Equation (10.9), we obtain

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$$\frac{dq}{dt} = \frac{d\psi_c}{de}\frac{de}{dt} \tag{10.10}$$

Defining reversible flow on the capacitor

$$f_{\text{reversible}} \equiv \frac{dq}{dt} \tag{10.11}$$

and capacitance

$$C \equiv \frac{d\psi_c}{de} \tag{10.12}$$

Equation (10.10) can be rewritten in the form

$$f_{\text{reversible}} = C\frac{de}{dt} \tag{10.13}$$

where e is the unique potential characterizing the capacitor. To cite a concrete example, let us assume that the concentration c_i of the ith component in a mixture is given as a unique function of its chemical potential, i.e.

$$c_i = c_i(\mu_i) \tag{10.14}$$

Expressing the flow J_i of the ith species as dc_i/dt, we can write

$$J_i = \frac{dc_i}{dt} = \frac{dc_i}{d\mu_i}\frac{d\mu_i}{dt} \tag{10.15}$$

The generalized capacitance C_i in this case thus would be given by

$$C_i = \frac{dc_i}{d\mu_i} \tag{10.16}$$

Now expressing μ_i as

$$\mu_i \approx \mu_i^0 + RT \ln c_i \tag{10.17}$$

where μ_i^0 is the reference value of the μ_i, Equation (10.16) would be read as

$$C_i \approx \frac{c_i}{RT} \tag{10.18}$$

where R is the gas constant. In the general case, the concentration c_i will depend upon the chemical potentials of all other components j, including i. For such a situation

$$J_i = \sum_j C_{ij}\frac{d\mu_i}{dt} \tag{10.19}$$

where C_{ij} is the capacitance matrix defined as

$$C_{ij} = \left(\frac{\partial c_i}{\partial \mu_i}\right)_{T,\mu_k} \tag{10.20}$$

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An examination of Equation (10.35) reveals that the relaxation time τ for the membrane process is of the same form as in electrical networks:

$$\tau = \frac{\mathbf{R}_m C_m}{2} \tag{10.36}$$

The magnitude or $\mathbf{R}_m$ for an ideal permeation process as evaluated from Fick's first law of diffusion and Equation (10.17) is

$$\mathbf{R}_m = \frac{RT\Delta x}{c_i D_m} \tag{10.37}$$

where Δx is the thickness of the membrane, and D_m, the diffusion coefficient within the membrane. The magnitude of the membrane capacity C_m for a membrane of thickness, Δx, according to Equation (10.18), can be written as

$$C_m = \frac{c_i \Delta x}{RT} \tag{10.38}$$

Substituting the values of $\mathbf{R}_m$ and C_m in Equation (10.36), we get the well-known Einstein's equation for relaxation time

$$\tau = \frac{(\Delta x)^2}{2D_m} \tag{10.39}$$

The model presented above (Figure 10.2) is not adequate to represent anisotropic membranes, e.g. the anisotropic cellulose acetate membranes prepared using evaporation technique or those used in reverse osmosis operation.

In the case of anisotropic cellulose acetate membranes prepared by the evaporation technique, it has been pointed out that the anisotropic character of such membranes may be due to the fact that by using the evaportation technique, one is likely to get a membrane of graded porosity. The membrane of graded porosity can be imagined to consist of a large number of layers of membranes of varying porosity arranged in series. This implies that such membranes would have conical convergent pores instead of symmetrical cylindrical pores. The situation is depicted in Figure 10.3. The arrangement of the resistive elements in the network shown in Figure 10.2(b) implies that the dissipation of energy takes place only during the flow through the channels. The fact that the magnitudes of the resistive elements in the network shown in Figure 10.2(b) are equal implies that the pores are cylindrical. The assumption that the dissipation of energy takes place only during flow through the channels is not quite true, because some of the energy is always wasted in the inter-channel region. This additional postulate together with the fact that in the case of membrane having conical channels the resistance to flow as viewed from one side of the membrane is not equal to the resistance as viewed from the other side of the membrane, which makes the dissipation of energy at the entrance and at the exit unequal, can be utilized to generalize the network shown in Figure 10.2(b).

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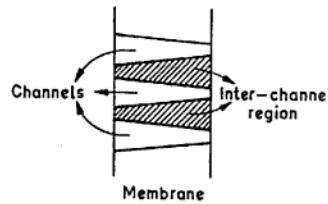

Figure 10.3 A membrane having conical channels.

The generalized version of the network which describes the anisotropic membrane is shown in Figure 10.4. The resistance $\mathbf{R}_1$ and $\mathbf{R}_4$ in Figure 10.4 account for the dissipation of energy in the inter-channel region and the resistances $\mathbf{R}_2$ and $\mathbf{R}_3$ represent the dissipation of energy at the entrance and at the exit during flow through the conical channels of the membrane. It is easy to see that the magnitude of the outflowing current I_0 for a particular value of the driving force changes when the direction of the driving force is reversed, i.e.

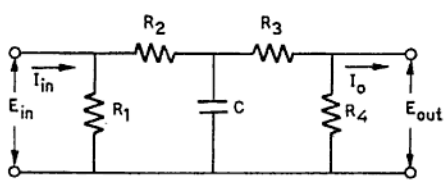

Figure 10.4 Network representation of an anisotropic membrane systems; R_1, R_2, R_3 and R_4 are resistances and C is the capacitance.

$$\bar{I}_o = \frac{E_{in} - E_{out}}{\mathbf{R}_2 + \mathbf{R}_3} - \frac{E_{out}}{\mathbf{R}_4} \tag{10.40}$$

and

$$\bar{I}_o = \frac{E_{in} - E_{out}}{\mathbf{R}_2 + \mathbf{R}_3} - \frac{E_{out}}{\mathbf{R}_1} \tag{10.41}$$

In the case of membranes having cylindrical channels, we have $\mathbf{R}_1 = \mathbf{R}_4$ and $\mathbf{R}_2 = \mathbf{R}_3$ making $\bar{I}_o = \bar{I}_o$. If such an anisotropic membrane system is allowed to age, the concentration on the two sides of the membrane would ultimately become equal, which means $E_{in} = E_{out} = E$. This, however, does not imply the condition of no-net flux. The net flux from Equations (10.40) and (10.41) can be written as

$$\bar{I}_o - \bar{I}_o = E\left(\frac{1}{\mathbf{R}_1} - \frac{1}{\mathbf{R}_4}\right) \tag{10.42}$$

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A parallel composite membrane consisting of two homogeneous membrane elements, say a and b, is schematically represented in Figure 10.5(a). Let us now invoke the assumptions made by Kedem and Katchalsky in their theory of the permeability of parallel composite membranes. The flows are assumed to be perpendicular to the membrane surface. The forces considered are differences of potential acting across the membrane and since the same compartment maintains contact with both membrane elements on each side of the membrane, the same force which operates on the parallel composite membrane is also operative on both the constituent membrane elements. This means that the forces are perpendicular to the membrane surface and that no lateral forces have to be considered and hence no lateral flows creating internal circulations need to be taken into account. Thus, the total flow through the parallel composite membrane is built up additively of the elementary contributions. The linear relationship between fluxes and forces is assumed to be valid for the parallel composite membrane as well as for the constituent membrane elements. In view of the assumptions listed above, the parallel composite membrane system can be represented by the networks shown in Figures 10.5(b) and 10.5(c). Utilizing the procedure outlined above and making use of the junction rules, the governing state equations can be written as

$$\frac{d\mu_a}{dt} = \frac{2}{\mathbf{R}_a C_a}\left[\langle\mu\rangle - \mu_a\right] \tag{10.43}$$

and

$$\frac{d\mu_b}{dt} = \frac{2}{\mathbf{R}_b C_b}\left[\langle\mu\rangle - \mu_b\right] \tag{10.44}$$

from which it is obvious that the parallel composite membrane system will have two relaxation times given by

$$\tau_a = \frac{\mathbf{R}_a C_a}{2} \tag{10.45}$$

and

$$\tau_b = \frac{\mathbf{R}_b C_b}{2} \tag{10.46}$$

This is in keeping with the physical reality. The time required by the two constituent membrane elements to become saturated with the permeant would be different and hence the constituent membrane element that requires longer time to become saturated with the permeant would determine the relaxation time for the total parallel composite membrane. Thus, if $\tau_a > \tau_b$, τ_a would be the relaxation time for the parallel membrane.

Let us now take up the case of a series composite membrane. A series composite membrane consisting of two homogeneous constituent membrane elements, say a and b, is schematically depicted in Figure 10.6(a). In this case also, let us bear in mind the assumptions made by Kedem and Katchalsky in their theory of the permeability of series composite membranes. Relevant among these for the present discussion are the following. All flows passing through the membrane are assumed to be perpendicular to the membrane. Flows through the series composite

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membrane as well as through the constituent membrane elements are adequately described by the linear relationships between fluxes and forces. The potentials of the thermodynamic driving forces are assumed to be continuous across all boundaries in the system. This condition, first formulated by Kirkwood, means that approaching any point in the system from the right or the left leads to the same potential. The physical reason for this is that if the transition layer between the two neighbouring phases (the two constituent membrane elements in the present case) is infinitely thin, its resistance to flow will be zero. Hence, if the potential difference across the transition layer does not vanish, infinite local flow will develop. What is implied, therefore, is that there cannot be a potential drop across the transition boundary within the series composite membrane. In view of these assumptions, the series composite membrane can be represented by the network shown in Figures 10.6(b) and 10.6(c). It is easy to see that the relaxation time in the case of a series membrane would be given by the equation

$$\tau_s = \frac{(\mathbf{R}_a + \mathbf{R}_b)(C_a + C_b)}{2} \tag{10.47}$$

or

$$\tau_s = \tau_a\left(1 + \frac{C_b}{C_a}\right) + \tau_b\left(1 + \frac{C_a}{C_b}\right) \tag{10.48}$$

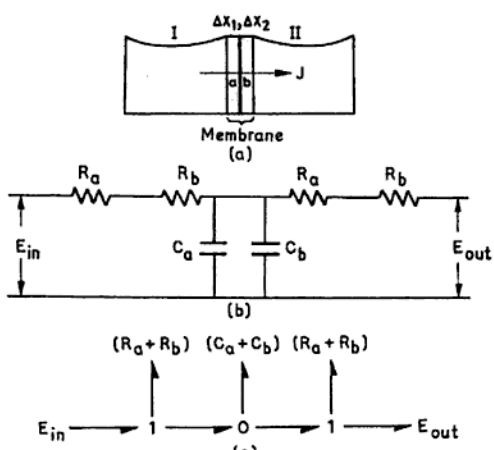

Figure 10.6 (a) A series composite membrane; *a* and *b* represent two constituent membrane elements; (b) network representation of the series membrane shown in (a); (c) bond graph representation of the network shown in (b).

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Let us begin the analysis by examining the middle zero junction to which a coupling force X_c and a corresponding coupling flow J_C have been assigned. The linear constitutive relationship between X_C and J_C may be written as

$$X_c = \mathbf{R}_c J_c \tag{10.49}$$

Now, utilizing Equation (10.26) defining the transducer and keeping in mind that all forces on a zero junction are equal, it is easy to see that the forces entering the two transducers in Figure 10.7 are X_c/r_A and X_c/r_B, where r_A and r_B are the transducer moduli for A and B respectively.

Applying KVL to the one junction for A (Figure 10.7), we can write

$$\mu_A^{\mathrm{I}} - \mu_A^{\mathrm{II}} = \Delta\mu_A = X_A + \frac{X_c}{r_A} \tag{10.50}$$

Similarly,

$$\mu_B^{\mathrm{I}} - \mu_B^{\mathrm{II}} = \Delta\mu_B = X_B + \frac{X_c}{r_B} \tag{10.51}$$

Utilizing the linear constitutive relations

$$X_A = \mathbf{R}_A J_A \tag{10.52}$$

and

$$X_B = \mathbf{R}_B J_B \tag{10.53}$$

for the diffusional resistance $\mathbf{R}_A$ and $\mathbf{R}_B$ respectively and the relation (10.49), Equations (10.50) and (10.51) can be written as

$$\Delta\mu_A = \mathbf{R}_A J_A + \frac{\mathbf{R}_C J_C}{r_A} \tag{10.54a}$$

$$\Delta\mu_B = \frac{\mathbf{R}_C J_C}{r_B} + \mathbf{R}_B J_B \tag{10.54b}$$

Since the flows on the zero junction (Figure 10.7) are related by the equation

$$J_C = \frac{J_A}{r_A} + \frac{J_B}{r_B} \tag{10.55}$$

the set of Equations (10.54) can be transformed into

$$\Delta\mu_A = \left(\mathbf{R}_A + \frac{\mathbf{R}_C}{r_A^2}\right) J_A + \frac{\mathbf{R}_C}{r_A r_B} J_B \tag{10.56a}$$

$$\Delta\mu_B = \frac{\mathbf{R}_C}{r_A r_B} J_A + \left(\mathbf{R}_B + \frac{\mathbf{R}_C}{r_B^2}\right) J_B \tag{10.56b}$$

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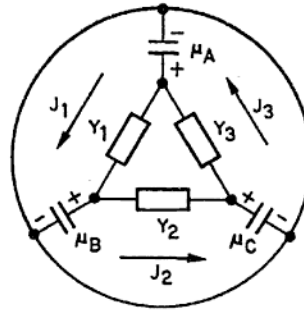

Figure 10.12 Network representation of the triangular isomerization reaction shown in Figure 10.11.

where x denotes the mole fraction of the species denoted by the subscript. The entropy production σ at a certain temperature T for the system shown in Figure 10.11 for the near equilibrium region, is given by Equation (8.158), i.e.

$$T\sigma = J_1A_1 + J_2A_2 + J_3A_3 \tag{8.158}$$

Since the relation

$$A_1 + A_2 + A_3 = 0$$

holds among the affinities, Equation (8.158) can be transformed into

$$T\sigma = (J_1 - J_3)A_1 + (J_2 - J_3)A_2 \tag{8.159}$$

The new fluxes now are $(J_1 - J_3)$ and $(J_2 - J_3)$ and the new conjugate forces are A_1 and A_2 respectively. Each of the three reactions (1), (2) and (3) of the reaction scheme shown in Figure 10.11 can be represented by a network of the type shown in Figure 10.9 and the total triangular isomerization reaction (Figure 10.11) can be shown by a closed network of the type shown in Figure 10.12. Since the measurable quantities in the triangular isomerization reaction are $-dx_A/dt$ and dx_C/dt, it is more profitable to consider the alternative choice of fluxes and forces given by Equation (8.159) for network representation. This will be given by the two-port network shown in Figure 10.13, from the nodal analysis of which we can write

$$-\frac{dx_A}{dt} = J_A = L_{11}A_1 + L_{12}A, \qquad \frac{dx_c}{dt} = J_c = L_{21}A_1 + L_{22}A_2 \tag{10.71}$$

where

$$L_{11} = Y_1 + Y_2, \qquad L_{12} = Y_2, \qquad L_{21} = Y_2, \qquad L_{22} = Y_2 + Y_3$$

The validity of Onsager's relations is again apparent from Equations (10.71). There can be good deal of exercises on the network thermodynamic modelling of transport processes including chemical reactions. Readers may refer to the review

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by Oster, Perelson and Katchalsky, review by Russell Paterson and the monographs by Schnakenberg and by A.R. Peacocke for a fuller account.[1]

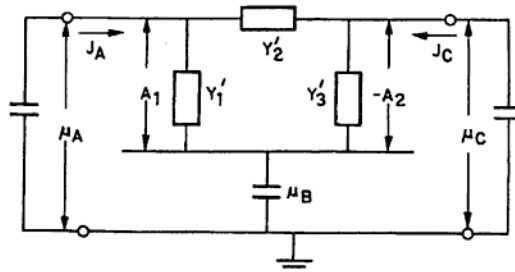

Figure 10.13 Two-port network describing the triangular isomerization reaction shown in Figure 10.11 for the alternative choice of fluxes and forces given by Equation (8.159).

QUESTIONS

1. What does the adjective 'bond' in 'bond graph' signify? List the main features of bond graph representation.
2. What does the element transducer (TD) stand for? What is the significance of transducer modulus? Give one example where it can be used with advantage.
3. What do the following symbols imply

$$\text{(a)} \overset{e}{\underset{f}{\rightharpoonup}} R \qquad \text{(b)} \overset{e}{\underset{f}{\leftharpoonup}} R$$

   Write the defining equations and their physical significance.
4. Give the bond graph representation of the enzymes reaction

$$E + S \rightleftharpoons ES \rightleftharpoons E + P$$

   E, S, ES and P stand for enzyme, substrate, enzyme-substrate complex and product, respectively.
5. How are 0-junction and 1-junction symbolically represented? Write the defining equations to show that they lead to KCL and KVL.

---

1. Oster, C.G., Perelson, A.S. and Katchalsky, A., *Q. Rev. Biophys.*, 6 (1973).
   Patterson, R. in *Membrane Structure and Function*, edited by E.E. Bittar, Wiley, 1980, Ch. 1
   Schnakenberg, J., *Network Thermodynamic Analysis of Biological Systems*, Springer-Verlag, Berlin, 1977.
   Peacocke, A.R., *The Physical Chemistry of Biological Organization*, Clarendon Press, Oxford, 1983, Ch 3.

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6. How will the bond graph shown in Figure 10.2 get modified when the condition of steady state flow through the membrane is reached?
7. What is meant by chemical capacitance? Explain with examples.
8. What essentially will be the difference between the bond graphs for diffusion through (1) a membrane having cylindrical pores and (2) a membrane having conical pores.
9. Generate the bond graph for the reaction

$$n_1 x + n_2 y \rightleftharpoons n_3 z$$

10. Constitutive relationships are in fact relationships between KCL variables and KVL variables. Explain with examples.

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Chapter 11

Causality Principle in Non-equilibrium Thermodynamics*

Causality principle is at the core of philosophy of science and scientific method and temper. Its philosophical implications have been discussed in sufficient detail in literature—both western and Indian. Interested readers may look into the several references cross-referred in Professor Rastogi's article cited here as a footnote. Broadly speaking, according to the causality principle, "Every effect should have a cause". In other words, there cannot be an effect without a cause. The causality principle is one of the most sacred principles of science like the conservation laws, e.g. conservation of mass, energy, etc. which should never be violated. Therefore, if we come across an effect without a cause, the scientific method and temper demand that we should investigate its cause rather than calling it a miracle. Miracle, in fact, is an effect whose cause is not apparent. For a society having scientific temper, miracles do not deserve to be true—believing in miracles, therefore, is antiscientific.

The phenomenological relations between fluxes and forces, which are one of the basic components of the formalism of non-equilibrium thermodynamics, are in fact cause–effect relationships. Let us see how?

When a single force and a single flux are involved, the phenomenological relationship can be written as follows:

$$O = LI \tag{11.1}$$

where I denotes the set of stimuli or inputs and O stands for the responses or outputs. Here L summarizes the property of the system, which is considered to be more or less a black box. The 'mechanism' connecting O and I is left unspecified. If there is a set of responses, O_1 and O_2, due to two inputs I_1 and I_2, the phenomenological relation is written as

$$O_1 = LI_1 + MI_2 \tag{11.2}$$

$$O_2 = PI_1 + QI_2 \tag{11.3}$$

*This chapter is based on the article published by Prof. R.P. Rastogi in the *J. Scient. Ind. Res.*, 40 (1981) 565–570.

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where M and P depend on the system which is again considered to be a black box. In the linear range, the fluctuation theory and the principle of microscopic reversibility lead to the famous Onsager reciprocity relation,

$$M = P \tag{11.4}$$

The relation of Eq. (11.4) is obtained using the principles of statistical mechanics and probability, based on the so-called concept of translucid box theory[1]. We shall elaborate these ideas in the following sections.

11.1 FLUX–FORCE RELATIONSHIP—TRANSPORT EQUATIONS

The basis of the phenomenological approach is the conventional equations of heat flow, electric current and fluid flow. In a general way, the transport equations can be written as

$$J_Z = -B\frac{\partial \theta}{\partial Z} \tag{11.5}$$

where J_Z is the quantity transported per cm^2 per second in the Z-direction, B is the proportionality constant, and $\dfrac{\partial \theta}{\partial Z}$ is the gradient of some parameter θ in the Z-direction. When the three-dimensional case is being considered, Eq. (11.5) can be written as

$$J = -B \text{ grad } \theta \tag{11.6}$$

More specifically, for heat flow, electric current, etc. the explicit transport equations are written as enumerated below:

Heat flow:

$$J_Z = -K_T\frac{\partial T}{\partial Z} \qquad \text{(Fourier's law)} \tag{11.7}$$

Electric current:

$$J_Z = -x\frac{\partial \phi}{\partial Z} \qquad \text{(Ohm's law)} \tag{11.8}$$

Fluid flow:

$$J_Z = -K\frac{\partial P}{\partial Z} \qquad \text{(Poiseulle's law)} \tag{11.9}$$

$$J_Z = -D\frac{\partial C}{\partial Z} \qquad \text{(Fick's law)} \tag{11.10}$$

---

[1] Bunge, M., *The Critical Approach to Science and Philosophy*, Free Press of Glencoe; Collier—Macmillan, London, 1964, Chap. 16.

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where K_T is the thermal conductivity coefficient, x is the electrical conductivity, K is the frictional coefficient related to viscosity, D is the diffusion coefficient, $\frac{\partial C}{\partial Z}$ and $\frac{\partial \phi}{\partial Z}$ are respectively the concentration gradient and potential gradient, and T and P denote the temperature and pressure respectively. K_T, D, and K for gases can be estimated from kinetic theory. However, D for liquids can be estimated from experiments alone.

Generalizing the above results, we can write the relation

$$J = LX \tag{11.11}$$

where J is any flux and X is the gradient of the corresponding force, which would certainly be true for the thermodynamic fluxes and forces. This is supported by overwhelming experimental evidence collected in the past few decades. Here, L is the phenomenological coefficient and would usually be scalar in character. It is obvious that if J and X are vectorial in character, L would still be a scalar quantity.

It is generally believed that mass flow is driven by the concentration gradient or pressure gradient. However, it is known that in thermo-osmosis[†‡] and electro-osmosis, mass flux of a fluid is driven by temperature difference and potential difference and experimentally it is found that in the absence of pressure difference in the case of a single fluid across a membrane of thickness δZ

$$J_Z = E\left(\frac{\delta T}{\delta Z}\right) \qquad \text{(for thermo-osmotic flux)} \tag{11.12}$$

$$J_Z = F\left(\frac{\partial \phi}{\partial Z}\right) \qquad \text{(for electro-osmotic flux)} \tag{11.13}$$

E and F may respectively be called thermo-osmotic and electro-osmotic permeability. Similarly, when the potential difference $\Delta\phi$ across the membrane is kept zero, the streaming current is found to be related to $\frac{\partial P}{\partial Z}$ in the following manner:

$$I = G\left(\frac{\partial P}{\partial Z}\right) \qquad \text{(for streaming current)} \tag{11.14}$$

where G is the phenomenological coefficient.

In chemical reactions, the reaction rate J_c is a function of affinity A and close to equilibrium, i.e.

$$J_c = L_c A \tag{11.15}$$

where L_c is the corresponding phenomenological coefficient. Whereas Eqs. (11.7–11.10) are valid for large values of the forces, Eqs. (11.12–11.15) have a much

---

† See R.P. Rastogi and Kehar Singh, *Trans. Faraday Soc.*, 62 (1966) 1754.

‡ R.P. Rastogi, R.L. Blokhra and R.K. Agarwal, *Trans. Faraday Soc.*, 60 (1964) 1384.

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smaller range of validity. The linear relation between the chemical reaction rate and the affinity has a still smaller range of validity.

11.2 TRANSPORT EQUATION FOR COUPLED PROCESSES

Transport equations for uncoupled processes have been discussed in Section 11.1. In nature, most of the processes are coupled unless the coupling is very weak. From a purely phenomenological angle, it was suggested that for such transport processes if there are n coupled fluxes and n corresponding forces, the phenomenological equations may be written as

$$J_i = \sum L_{ik} X_k \qquad (i, k = 1, 2, \ldots, n) \tag{11.16}$$

It should be noted that 'causes' such as temperature gradients are not real powers or propensities operating in nature. These have to be looked upon as subsumption under a general law represented by Eq. (11.16), where L_{ii}, L_{kk} are called straight coefficients and L_{ki}, L_{ik} are cross coefficients. Thermal diffusion is a coupled process and coupling of mass flow and heat flow occurs in this phenomenon. Similarly, coupling of mass flow and electric current occurs in electro-kinetic phenomena. Experimental studies and the kinetic theory of phenomena confirm that this would be so. In a general way, the forces of a particular tensorial order will couple only with forces of the same tensorial order. Thus,

$$\vec{J}_i = \sum L_{ik} \vec{X}_k \tag{11.17}$$

and

$$J_i = \sum L_{ik} X_k \tag{11.18}$$

where the quantities with arrows denote the vectorial quantities, such as heat flow and mass flow, while the quantities with no arrow denote scalar quantities, such as chemical reactions. Chemical reaction is a scalar cause and it cannot give rise to a vector effect. Chemical affinity cannot produce a directed heat flow. Therefore, the interference coefficient must necessarily be zero.

11.3 TEMPORAL SEQUENCE

Experiments on thermo-osmosis and electro-osmosis clearly demonstrate the temporal sequence of flux and force. In thermo-osmotic experiments, mass flux is observed after the imposition of temperature gradient across the membrane. In the same way, in electro-osmotic experiments, mass flux is observed only after the potential difference is imposed across the membrane.

We can define J_i of Eq. (11.16) as

$$J_i = \overline{\frac{a_i(t+\tau) - a_i(t)}{\tau}} \tag{11.19}$$

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where a_i denotes the deviation of the characteristic parameters at time $(t + \tau)$ and t respectively. A pertinent question is: what is the range of τ? It has been argued that τ is much greater than the time interval between two successive molecular collisions. However, τ is much smaller than the regression time τ_r of a fluctuation.

When fluxes and forces are sufficiently small, we can write[2]

$$J(t) = \sum_{k=1}^{n} \int_{-\infty}^{\infty} L_{ik}(t-t')X_k(t')dt \tag{11.20}$$

where t' is the time when force is applied and t is the time when flux is generated. Thus, $(t - t')$ is equal to τ. It is easy to see that J_i would be a function of t, while L_{ik} would be a function of τ. Since the effect cannot appear before the appearance of a cause,

$$L_{ik}(t-t') = 0 \tag{11.21}$$

where $t < t'$. On the other hand, when $t > t'$

$$\int_{0}^{\infty} L_{ik}(\tau)d\tau < \infty$$

Since the integrals must exist and must be finite**, Eqs. (11.20) and (11.21) are the basic causality conditions.

11.4 PLURALITY OF CAUSES

Non-equilibrium thermodynamics starts with the premise that an effect can arise from a number of causes††. For example, mass flow can be generated by pressure difference, ΔP, as well as by temperature difference, ΔT, and potential difference, $\Delta\phi$, giving rise to different phenomena as shown below:

Effect	*Cause*	*Phenomenon*
Mass flow	(i) ΔP	(i) Poiseulle's flow
	(ii) ΔT	(ii) Thermo-osmosis
	(iii) $\Delta\phi$	(iii) Electro-osmosis

---

[2] de Groot S.R. and P. Mazur, *Non-equilibrium Thermodynamics*, North Holland and Publishing Co., Amsterdam, 1963, p.143.

** To be antecedent of effect (flux), it is necessary that the cause (force) must be separated from the effect in time for howsoever small a period it might be. In the above paragraphs, this interval is τ. Nyaya Vaiseshika, however, regards a break of one moment between cause and effect.

Pa'qamao xaNa inagau-Na eva GaT]%pQato gauNaoBya: pUva-Baavalit

See *Tarka-Bhasa of Kisavmisra*, Hindi Transl. and commentary by Acharya Visvesara Ch. S.S. Banaras, 1953 (Tarka-Bhasa p.33).
see also, Bhartiya, M.C., *Causation in Indian Philosophy*, Vimal Prakashan, Ghaziabad, 1973, p.147.

†† "An effect, according to Budhists, is not the result of a single cause, but of many causes working together....The totality of causes is called Samagri"

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an example, let us consider the phenomenon of thermo-osmotic concentration difference[3]. When a temperature difference ΔT is maintained across a membrane separating two chambers containing a binary gaseous mixture, a concentration difference ΔC_i of the component i is set up. Is ΔT the cause of ΔC_i? Both are forces (causes) in the sense we have discussed above. Where has the mass flux associated with both ΔT and ΔC_i disappeared? A closer scrutiny suggests that the causal sequence would be

$$\Delta T \rightarrow \begin{cases} \text{Heat flow} \\ \text{Mass flow} \rightarrow \Delta C \end{cases}$$

so that eventually, the mass flow becomes the cause of concentration difference.

In the same manner, when a concentration difference is created in a fluid system, the temperature difference is generated. This happens for both gaseous and liquid mixtures and the phenomenon is called Dufore effect[4,5]. The sequence of cause and effect is similar in this case. The concentration difference generates heat flow which generates the temperature difference. Both the uniformity and universality of causes is questioned in these phenomena.

This means that the role of cause and effect can be reversed, depending on the situation. Implicitly this point is taken care of when phenomenological equation is written in the alternative form

$$X = RJ \tag{11.22}$$

where R is the reciprocal matrix of L.

11.8 AUTOCATALYSIS AND CAUSALITY RELATION

Far from equilibrium, in chemical reactions involving sequential changes having one or two autocatalytic steps, periodic changes in the concentration of some intermediates and dissipative structures are observed. Since such phenomena are analogues of biological phenomena and these appear when an autocatalytic step is involved, a discussion of autocatalysis from the viewpoint of causality principle is presented. The typical Lotka-Volterra scheme is represented as follows[6]:

$$A + X \rightleftharpoons 2X$$
$$X + Y \rightleftharpoons 2Y$$
$$Y \rightleftharpoons E$$

Both X and Y are produced autocatalytically. It is obvious that X is the cause of itself and Y also is the cause of itself. It seems that the concept of Causality Principle is lost in autocatalysis. For discussion in this section we have the material cause in mind.

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[3] R.P. Rastogi and Byas Misra, *J. Membr. Sci.*, 4(1978)1.
[4] R.P. Rastogi and G.L. Madan, *J. Chem. Phys.*, 43(1965) 4179.
[5] R.P. Rastogi and G.L. Madan, *Trans. Faraday Soc.*, 62(1966) 3325.
[6] See G. Nicolis and I. Prigogine, *Self Organization in Non-equilibrium System*, Wiley, New York, 1977.

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product species initially present in the reaction mixture interacts with some of the reactants to produce a species, which on reaction with another reactant produces more of the original product species. Thus, there is a causal sequence, but if the intermediate cause is eclipsed, the causal relation would seem to break down.

11.10 NECESSARY AND SUFFICIENT CONDITION FOR A CAUSAL SEQUENCE

It is a practice now to discuss organic and inorganic reactions in terms of the reaction mechanism. These are usually postulated on the basis of the number of experimental observations. "One can today easily demonstrate that there can be no valid derivation of a law of nature from any finite number of facts"[8]. Evidently a philosophical question arises: what are the necessary and sufficient conditions for a reaction mechanism to be valid? This question has not been answered satisfactorily. Nowadays, chemists talk of a 'plausible mechanism', because no mechanism can be proved to be ultimately true.

Attempts have been made to illustrate the dynamical evolution of life and dynamical evolution of species by Prigogine† by postulating such mechanisms. Again on the basis of the above arguments these cannot be considered final.

According to Popper[9], a theory may be scientific even if there is not a shred of evidence in its favour, and it may be pseudo-scientific even if all the available evidence is in its favour. In other words, the scientific or non-scientific character of a theory can be determined independently of the facts. A theory is 'scientific' if one is prepared to specify in advance a crucial experiment (or observation) which can falsify it, and it is pseudo-scientific, if one refuses to specify such a 'potential falsifier[8]*'. Probably, Popper's feasibility criterion is the solution to the problem of selecting the right mechanism when we use the word 'mechanism' in place of 'theory'. For the present discussion, mechanism and causal sequence have the same connotation.

Thus summing up Popper's rule that "We are not to abandon the search for universal laws and for a coherent theoretical system, nor ever give up our attempts to explain causality and kind of events we can describe" stands supported. Non-equilibrium thermodynamics is essentially based on the flux–force relationship, which, in turn, is based on the concept of causality. Irreversible thermodynamics

---

[8] See "The Methodology of Scientific Research Programs, Philosophical papers, Vol. 1"., edited by John Warral and Gregory Curne, Cambridge University Press, 1978, p.3.

† See footnote 6 on page 302.

[9] K.R. Popper, *The Logic of Scientific Discovery*, Hutchinson and Co. London, 1959, pp. 59,61.

*Some interesting falsifiers which smash some of the accepted hypotheses are as follows:

(1) The hypothesis that noble gases do not form chemical compounds at all was falsified in 1962 by Neil Bartlett's discovery of the formation of xenon-hexafluoro platinate.

(2) In the same way, the concept that nitrogen molecules are inert to organic molecules has been falsified by the studies on the mechanism of diazonation which shows that the reaction proceeds as follows and the reverse reaction in the first step does take place (see Chemistry in Britain 16 (1980) 257)

$$C_6H_5N_2^+ \rightleftharpoons C_6H_5^+ + N_2 \xrightarrow[+\,H_2O]{\text{Fast}} C_6H_5\overset{+}{O}H_2 \xrightarrow[-\,H_2O]{} C_6H_5OH + H_3O^+$$

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Answers

Chapter 2

2.1 $W_1 = -2.31$ kJ, $W_2 = -2.31$ kJ, $W_3 = -2.31$ kJ

2.2 $C_P = 29.9$ JK^{-1} mol^{-1}, $C_V = 21.6$ JK^{-1} mol^{-1}

2.3 $W = -455$ J

2.4 -90 Pa m^3 or -90 J

Chapter 3

3.1 -850 kJ,

3.2 4.5×10^5 J

3.3 -1.72 kJ

3.4 -1365.5 kJ

3.7 -3267.6 kJ mol^{-1}

3.8 -223.5 kJ

3.9 -285.65 kJ mol^{-1}

3.10 -72.01 kJ mol^{-1}

3.11 605 kJ mol^{-1}

3.12 687.8 kJ mol^{-1}

Chapter 5

5.1 0.33

5.2 0.134

5.4 5.8 JK^{-1}

5.5 14.56 JK^{-1}

5.6 1.048 kJ K^{-1}

5.7 (a) 4 (b) $\frac{1}{4}$ (c) 18, $\frac{18}{4}$ (d) 12

5.8 10^{24} times

5.9 -15.95 J mol^{-1}

5.10 $\Delta G = -3726.5$ J, $\Delta S = 12.51$ JK^{-1}

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5.11 $\Delta A = -812.63$ kJ, $\Delta G = -817.6$ kJ, $w = -812.63$ kJ

5.12 -6.34 JK^{-1}

5.13 $\Delta G = -687.52$ kJ; ΔG negative, spontaneous reaction

5.14 309.5 JK^{-1} mol^{-1}

5.15 -2058.2 kJ

5.16 2042 K

5.17 89.7°C

5.18 74.9°C, 32.83 kJ mol^{-1}

5.19 (i) 572 kJ (ii) 474.26 kJ

5.20 55.91 g/mol

5.21 257, i.e. S_8

5.22 0.75 K

5.23 1.94×10^{-3}

5.25 (i) $\Delta G° = -357$ kJ mol^{-1}, $K = 3.87 \times 10^{62}$ (ii) $\Delta G° = -90.71$ kJ mol^{-1}, $K = 7.95 \times 10^{15}$

5.26 $E°_{cell} = 1.0915$ V

5.27 0.0207 V

5.28 $E = 1.613$ V

5.30 0.0117 V, yes

Chapter 6

6.7 0.51 m mol kg^{-1}

6.8 $V^E = 0.145$ cm^3 mol^{-1}

6.9 $V = 60.62$ cm^3

6.10 (i) $a = 4\ m^3\gamma_\pm^3$, $a_\pm = 4^{1/3}\ m\gamma_\pm$

(ii) $a = 27\ m^4\gamma_\pm^4$, $a_\pm = (27)^{1/4}\ m\gamma_\pm$

6.11 (a) $a_\pm = 0.0113$, $m_\pm = 0.016$

(b) $a_\pm = 0.043$, $m_\pm = 0.079$

6.12 $K_f = 1.86$ $K{\cdot}kg{\cdot}mol^{-1}$

6.13 $T_f = -1.475$°C

6.14 $M = 44{,}030$

6.15 $\Pi = 0.58$ atm

6.16 $a_\pm = 0.402$, $a = 0.065$

6.17 $\gamma_\pm = 0.889$

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Chapter 7

7.1 7567560

7.2 30

7.3 13.38 JK^{-1} mol^{-1}

7.4 1.076×10^{-5}

7.5 14278 K

7.6 2.44×10^{9}

7.7 3716 J mol^{-1}

7.8 14.4 JK^{-1} mol^{-1}

7.9 S_t = 152.89 JK^{-1} mol^{-1}, G_t = −36.06 kJ mol^{-1}

7.10 107.65

7.11 S_r = 47.20 JK^{-1} mol^{-1}, G_r = −11.59 kJ mol^{-1}

7.12 8.47, 0.114, 1.53×10^{-3} and 2.06×10^{-5}, respectively

7.13 8.376 JK^{-1} mol^{-1}

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